A direct diagrammatic construction scheme for the inelastic propagator between simply excited states

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Abstract

We develop a direct diagrammatic construction scheme for the inelastic propagator, which describes inelastic scattering processes. Starting from the previously presented 'direct approach' to the inelastic propagator, which involves a higher-order elastic Green's function, we show how one can obtain the inelastic propagator for simple excitations without actually evaluating all the diagrams for the higher-order Green's function. The three cases where either the target molecule itself or its cation or anion is a closed-shell system are discussed. A generalization of the method to obtaining inelastic propagators between higher excitations is briefly addressed.

PACS numbers: 34.80.Gs, 03.65.Nk, 31.10.+z

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I. INTRODUCTION

It has been known for a long time now that elastic scattering of electrons by molecules can be treated successfully with the help of Green's functions. Already in [1], it was shown that the one-particle Green's function (also called *propagator*) obeys a Dyson equation, in which the self-energy is an optical potential [2] for the scattering. Nowadays, there is a multitude of methods for calculating the propagator for elastic scattering and consequently the scattering matrix, phase shifts and resonance energies (for some examples, see [3–9]).

On the other hand, not much work has been done on the use of Green's function methods in the even more important case of *inelastic* scattering. Some pioneering work in this direction was done by Csanak et al.[10, 11], but they did not develop formal inelastic equivalents to the elastic Green's function and the optical potential, which are so useful concepts in the treatment of elastic scattering. Such a formulation was achieved only in recent years, first for the scattering of *non-electronic* projectiles from molecular targets [12, 13], and afterwards also for the case where the projectile is indistinguishable from the target particles [14–16]. Also worthwhile mentioning is the work done on the treatment of inelastic scattering of electrons in the case that rotational and vibrational degrees of freedom of the target molecule are excited [17].

Recently, two systematic diagrammatic methods for explicitly evaluating the inelastic propagator for transitions between electronically excited states were developed, the *direct approach* and the *Dyson approach* [18]. Both methods are based on spectral representations of higher-order *elastic* Green's functions. From these, one can extract either the inelastic propagator directly, or generalized one-particle densities, which can be used to obtain the inelastic propagator from Dyson-like equations.

A drawback of these methods is that for obtaining the inelastic propagator (or the generalized densities, respectively) perturbatively, one first has to evaluate the Goldstone diagrams for the higher-order Green's functions and then extract the desired quantity from the results. Even in low orders of perturbation theory, already several hundred diagrams have to be considered, and extracting the inelastic propagators out of the various contributions to the higher-order Green's functions is also not an easy task (see the examples given in [18]). Hence it is desirable to construct a diagrammatic evaluation method for the inelastic propagator *directly*.

As a first step towards that goal, it was already pointed out in [18] that if one is interested only in the inelastic propagator for the simplest excitations (i. e. $1p$-, $1h$- or $1p1h$-excitations), only a considerable smaller number of diagrams has to be taken into account. We demonstrate in this work how also the second problem, the extraction of the inelastic propagator out of the various contributions, can be solved. This will lead to a diagrammatic construction method which gives the inelastic propagator between the simplest excitations itself, instead of only the higher-order Green's functions.

Section II first briefly summarizes the definitions of the inelastic propagator and of the higher-order elastic Green's function used in [18], and how one can obtain the former from the latter in the direct approach. We then go on developing our new method in section III and give Feynman rules for constructing and evaluating the diagrams for the inelastic propagator. This will be done for all three cases already addressed in [18], a neutral closed-shell target molecule as well as the cases of open-shell target molecules with closed-shell ions. Inelastic propagators for higher excitations will also briefly be discussed. Finally, section IV summarizes our results and addresses the possibility of applying our methods also in the Dyson approach. The appendix introduces some mathematical notation and contains a formal statement of the Feynman rules and their proof.

II. REVIEW OF THE DIRECT APPROACH

The inelastic propagator was defined in [15] by:

$$G_{pq}^{[M,N]}(\tau) = G_{pq}^{+[M,N]}(\tau) + G_{pq}^{-[M,N]}(\tau),$$

where

$$\begin{aligned} iG_{pq}^{+[M,N]}(\tau) &= \theta(\tau) < M|c_p(t)c_q^\dagger(t')|N > e^{i\Phi^{+[M,N]}(t,t')} \\ iG_{pq}^{-[M,N]}(\tau) &= -\theta(-\tau) < M|c_q^\dagger(t')c_p(t)|N > e^{i\Phi^{-[M,N]}(t,t')}, \end{aligned} \tag{1}$$

and the phases are

$$\begin{aligned} \Phi^{+[M,N]}(t,t') &= -(E^{[M]} - E^{[0]})t + (E^{[N]} - E^{[0]})t' \\ \Phi^{-[M,N]}(t,t') &= -(E^{[M]} - E^{[0]})t' + (E^{[N]} - E^{[0]})t. \end{aligned} \tag{2}$$

The c_p and $c_q^\dagger$ are the usual one-particle destruction and creation operators, $E^{[0]}$ is the energy of the ground state $|0>$, and the $E^{[M]}$ are the energies of the excited states $|M>$. The

part G^+ is called the particle component, whereas G^- is called the hole component of the inelastic propagator.

In [18], we also showed that in the cases of closed-shell ions, the ground state energy of the ion ($E^{[0^-]}$ if one considers a closed-shell anion, or $E^{[0^+]}$ for the case of a closed-shell cation) naturally appears in the phases instead of the ground state energy $E^{[0]}$ of the neutral molecule itself.

The definition given above is for the so-called 'natural' inelastic Green's function [15]. In [18], we discussed also the 'scattering-motivated' and the 'ionization-motivated' inelastic Green's functions. Here, we will concentrate on the first case only, for which we developed a straightforward method to construct the inelastic propagator. In the other two cases, this does not seem to be so easily possible.

A. Closed-shell neutral molecule

For the case of a closed-shell neutral molecule, the following six-point, four-times Green's function was used in the direct approach presented in [18]:

$$\begin{aligned} & iR_{pqrstu}(t_f,t,t',t_i) \\ = & -<0|\hat{T}\left[c_p^\dagger(t_f)c_q(t_f)c_r(t)c_s^\dagger(t')c_t^\dagger(t_i)c_u(t_i)\right]|0> \\ & +<0|\hat{T}\left[c_p^\dagger(t_f)c_q(t_f)c_r(t)c_s^\dagger(t')\right]|0><0|c_t^\dagger(t_i)c_u(t_i)|0> \\ & +<0|\hat{T}\left[c_r(t)c_s^\dagger(t')c_t^\dagger(t_i)c_u(t_i)\right]|0><0|c_p^\dagger(t_f)c_q(t_f)|0> \\ & +<0|\hat{T}\left[c_p^\dagger(t_f)c_q(t_f)c_t^\dagger(t_i)c_u(t_i)\right]|0><0|\hat{T}\left[c_r(t)c_s^\dagger(t')\right]|0> \\ & -2<0|c_p^\dagger(t_f)c_q(t_f)|0><0|\hat{T}\left[c_r(t)c_s^\dagger(t')\right]|0><0|c_t^\dagger(t_i)c_u(t_i)|0> . \end{aligned} \tag{3}$$

The time indices "f" and "i" mean "final" and "initial", respectively, and $\hat{T}$ denotes the usual time ordering operator. 24 time orderings are possible, which all depend only on the three time differences $\tau_f = t_f - t$, $\tau = t - t'$ and $\tau_i = t' - t_i$, or alternatively $\tau'_f = t_f - t'$, $\tau = t - t'$ and $\tau'_i = t - t_i$.

The component of R corresponding to $\tau_f > 0$, $\tau_i > 0$ and $\tau > 0$ was called $R^{(I)}$, whereas $R^{(II)}$ is the component of R with $\tau'_f > 0$, $\tau'_i > 0$ and $\tau < 0$. It was shown that Fourier transforming with respect to all three time differences leads to the following spectral repre-

sentations of these two components:

$$R^{(I)}_{pqrstu}(\omega_f,\omega_i,\omega) = \sum_{M\neq 0,N\neq 0} \frac{\rho^{[0,M]}_{pq}}{\omega_f-(E^{[M]}-E^{[0]})+i0^+}\frac{\rho^{[N,0]}_{tu}}{\omega_i-(E^{[N]}-E^{[0]})+i0^+} \cdot\Big[G^{+[M,N]}_{rs}(\omega)-\delta_{MN}G^{+[0,0]}_{rs}(\omega-(E^{[M]}-E^{[0]}))\Big] \quad (4)$$

and

$$R^{(II)}_{pqrstu}(\omega'_f,\omega'_i,\omega) = \sum_{M\neq 0,N\neq 0} \frac{\rho^{[0,M]}_{pq}}{\omega_f-(E^{[M]}-E^{[0]})+i0^+}\frac{\rho^{[N,0]}_{tu}}{\omega_i-(E^{[N]}-E^{[0]})+i0^+} \cdot\Big[G^{-[M,N]}_{rs}(\omega)-\delta_{MN}G^{-[0,0]}_{rs}(\omega-(E^{[M]}-E^{[0]}))\Big]. \quad (5)$$

Here, the *generalized one-particle densities* are defined by

$$\rho^{[N,M]}_{pq} =< N|c^\dagger_p c_q|M > . \quad (6)$$

The poles of the components $R^{(I)}$ and $R^{(II)}$ of the Green's function (in both ω_f and ω_i or ω'_f and ω'_i, respectively) are thus seen to be given by the energy differences between the excited states and the ground state of the system, and the residues of the double poles yield the inelastic propagators.

As explained in [18], for the perturbative evaluation of R it is convenient to write it using a matrix notation. We introduced vectors $\mathbf{T}_{tu}$ containing the generalized densities $\rho^{[N,0]}_{tu}$ for *fixed* t,u and matrices $\mathbf{G}_{rs}(\omega)$ for the propagators

$$G^{+[M,N]}_{rs}(\omega)-\delta_{MN}G^{+[0,0]}_{rs}\left(\omega-(E^{[M]}-E^{[0]})\right)$$

for *fixed* r,s (the vector and matrix indices run over the excited states). Further, we introduced the *diagonal* matrices $\mathbf{E}$ and $\mathbf{V}$, where the diagonal elements of $\mathbf{E}+\mathbf{V}$ are the energy differences $E^{[M]}-E^{[0]}$; $\mathbf{E}$ contains their leading-order contributions and $\mathbf{V}$ the higher orders. This enabled us to write:

$$R^{(I)}_{pqrstu}(\omega_f,\omega_i,\omega) = \mathbf{T}^\dagger_{qp}\frac{1}{\omega_f-\mathbf{E}-\mathbf{V}}\mathbf{G}_{rs}(\omega)\frac{1}{\omega_i-\mathbf{E}-\mathbf{V}}\mathbf{T}_{tu}. \quad (7)$$

An analogous expression also holds for $R^{(II)}$.

In any given order n of perturbation theory, $R^{(I)}$ receives various contributions. For the evaluation, it is then convenient to subdivide $\mathbf{T}$, $\mathbf{G}$, $\mathbf{E}$ and $\mathbf{V}$ into blocks, corresponding to the different types of excitations. In [18], we used superscripts 1, 2, etc., enclosed in square brackets, for denoting the contributions from $1p1h$-, $2p2h$- etc. excitations, e.g .$\mathbf{G}^{[1,1]}_{rs}$ for the

propagator between $1p1h-$states. The evaluation of $R^{(I)(1)}$, i. e., the first order contribution to $R^{(I)}$, using these methods was shown explicitly in [18].

If one is interested in the inelastic propagator in order n for $1p1h$-excitations, only one of the various summands which make up $R^{(I)(n)}$ is relevant:

$$\begin{aligned} R^{(I)(n)}_{pqrstu}(\omega_f,\omega_i,\omega) &= \mathbf{T}^{[1](0)\dagger}_{qp}\frac{1}{\omega_f-\mathbf{E}^{[1]}}\mathbf{G}^{[1,1](n)}_{rs}(\omega)\frac{1}{\omega_i-\mathbf{E}^{[1]}}\mathbf{T}^{[1](0)}_{tu}+\dots \\ &= \frac{n_p\bar{n}_q\left(G^{+[q\bar{p},t\bar{u}](n)}_{rs}(\omega)-\delta_{pu}\delta_{qt}G^{+[0-,0-](n)}_{rs}(\omega-E^{[q\bar{p}]}+E^{[0]})\right)\bar{n}_t n_u}{(\omega_f+\epsilon_p-\epsilon_q+i0^+)(\omega_i-\epsilon_t+\epsilon_u+i0^+)} \\ &\quad +\dots \end{aligned} \tag{8}$$

Here, ϵ_p denote the one-particle energies, and n_p are the occupation numbers of the orbitals, with $\bar{n}_p = 1 - n_p$. $G^{+[q\bar{p},t\bar{u}]}_{rs}$ is the particle component of the inelastic propagator between excitations which are on the Hartree-Fock level simply the states with a hole in orbital u and a particle in orbital t, or with a hole in orbital p and a particle in orbital q, respectively.

$R^{(I)(n)}$ can be obtained with the help of Feynman and Goldstone diagrams; for details, see [18]. We used the Hamiltonian

$$H = \sum_p \epsilon_p c^\dagger_p c_p + \sum_{pq} W_{pq} c^\dagger_p c_q - \frac{1}{2}\sum_{abcd} V_{abcd} c^\dagger_a c^\dagger_b c_c c_d \tag{9}$$

with the Hartree-Fock one-particle interaction

$$W_{pq} = -\sum_n V_{pn[qn]} n_n. \tag{10}$$

The quantities

$$V_{abcd} =< \phi_a(1)\phi_b(2)|V(1,2)|\phi_c(1)\phi_d(2) >$$

denote the matrix elements of the two-particle interaction with respect to the one-particle states $|\phi_a>$, and the abbreviation

$$V_{ab[cd]} = V_{abcd} - V_{abdc} = V_{abcd} - V_{bacd} = V_{[ab]cd}$$

is used for the antisymmetrized matrix elements.

As already argued in [18], a Goldstone diagram for order n which has an internal vertex at a time before t_i or after t_f can not contribute to the term shown in (8). Thus, there is a considerable reduction in the number of time orderings which have to be considered: only $(n+2)!/2$ (=1, 3, 12, ..., compared to $(n+4)!/4!$=1, 4, 20, ... in the original direct

approach) Goldstone diagrams are necessary to evaluate for every Feynman diagram and any given time ordering of the external vertices. We have then 2 Goldstone diagrams in zeroth order, 18 in first order, and 432 in second order.

The expression (8) will be our starting point for constructing a diagrammatic evaluation scheme for the inelastic propagator $G_{rs}^{[q\bar{p},t\bar{u}]}$ directly.

B. Closed-shell anion

This case is simpler than the treatment of closed-shell neutral molecules. Only a four-point, four-times inelastic Green's function is necessary in the direct approach:

$$\begin{aligned} iR_{pqrs}(t_f,t,t',t_i) \;=\; & - < 0^-|\hat{T}\left[c_p^\dagger(t_f)c_q(t)c_r^\dagger(t')c_s(t_i)\right]|0^- > \\ & + < 0^-|\hat{T}\left[c_p^\dagger(t_f)c_s(t_i)\right]|0^- >< 0^-|\hat{T}\left[c_q(t)c_r^\dagger(t')\right]|0^- > . \end{aligned} \tag{11}$$

The notation is as in the previous section. $|0^->$ denotes the ground state of the anion here.

As previously, 24 time orderings are possible, which all depend only on the three time differences $\tau_f = t_f - t$, $\tau = t - t'$ and $\tau_i = t' - t_i$, or alternatively $\tau_f' = t_f - t'$, $\tau = t - t'$ and $\tau_i' = t - t_i$. The components $R^{(I)}$ and $R^{II)}$ are defined in the same way as in the case of the closed-shell neutral molecule. The spectral representations are then:

$$\begin{aligned} R_{pqrs}^{(I)}(\omega_f,\omega_i,\omega) \;=\; & \sum_{M,N} \frac{x_p^{[M]\dagger}}{\omega_f - (E^{[M]} - E^{[0^-]}) + i0^+} \frac{x_s^{[N]}}{\omega_i - (E^{[N]} - E^{[0^-]}) + i0^+} \\ & \cdot \left[G_{qr}^{+[M,N]}(\omega) - \delta_{MN} G_{qr}^{+[0^-,0^-]}(\omega - (E^{[M]} - E^{[0^-]})\right]. \end{aligned} \tag{12}$$

and

$$\begin{aligned} R_{pqrs}^{(II)}(\omega_f',\omega_i',\omega) \;=\; & \sum_{M,N} \frac{x_p^{[M]\dagger}}{\omega_f' - (E^{[M]} - E^{[0^-]}) + i0^+} \frac{x_s^{[N]}}{\omega_i' - (E^{[N]} - E^{[0^-]}) + i0^+} \\ & \cdot \left[G_{qr}^{-[M,N]}(\omega) - \delta_{MN} G_{qr}^{-[0^-,0^-]}(\omega - (E^{[M]} - E^{[0^-]})\right], \end{aligned} \tag{13}$$

with the transition amplitudes

$$x_s^{[N]} =< N|c_s|0^- > . \tag{14}$$

The following matrix notation was very helpful for the diagrammatic evaluation in this case:

$$R_{pqrs}^{(I)}(\omega_f,\omega_i,\omega) = \mathbf{X}_p^\dagger \frac{1}{\omega_f - \mathbf{E} - \mathbf{V}} \mathbf{G}_{qr}(\omega) \frac{1}{\omega_i - \mathbf{E} - \mathbf{V}} \mathbf{X}_s, \tag{15}$$

and an analogous expression for $R^{(II)}$. Here, the vectors $\mathbf{X}_s$ contain the transition amplitudes $< N|c_s|0^- >$ for *fixed* s. The matrices $\mathbf{G}_{qr}$, $\mathbf{E}$ and $\mathbf{V}$ are as in the case of the closed-shell molecule, with the exception that $E^{[0^-]}$ has to be used instead of $E^{[0]}$. The matrices can be subdivided into blocks again, this time for the $1h$-, $2h1p$-, etc. excitations. We denoted them in [18] with superscripts 1, 2, etc. in square brackets.

In the perturbative expansion of this expression, various terms contribute, coming from the perturbative expansion of $\mathbf{X}$, $\mathbf{V}$ and $\mathbf{G}$. But if one is interested in the inelastic propagator for $1h$-excitations, only one term is of relevance:

$$\begin{aligned} R^{(I)(n)}_{pqrs}(\omega_f,\omega_i,\omega) &= \mathbf{X}^{[1](0)\dagger}_p \frac{1}{\omega_f - \mathbf{E}^{[1]}} \mathbf{G}^{[1,1](n)}_{qr}(\omega) \frac{1}{\omega_i - \mathbf{E}^{[1]}} \mathbf{X}^{[1](0)}_s + \dots \\ &= \frac{n_p \left(G^{+[\bar{p},\bar{s}](n)}_{qr}(\omega) - \delta_{ps} G^{+[0^-,0^-](n)}_{qr}(\omega - E^{[\bar{p}]} + E^{[0^-]}) \right) n_s}{(\omega_f + \epsilon_p + i0^+)(\omega_i + \epsilon_s + i0^+)} \\ &\quad + \dots \end{aligned} \tag{16}$$

where $G^{+[\bar{p},\bar{s}]}_{qr}$ is the particle component of the inelastic propagator between excitations which are on the Hartree-Fock level simply the states with a hole in orbital p or in orbital s, respectively.

The same argument as for the closed-shell neutral molecule applies here: for every given Feynman diagram, only the $(n+2)!/2$ Goldstone diagrams for which all internal vertices are between t_i and t_f contribute. Then we have 1 Goldstone diagram in zeroth order, 3 in first order, and 60 in second order (see [18]; the relevant Feynman rules were also given there). The expression (16) can then serve as the starting point for an evaluation of the inelastic propagator $G^{[\bar{p},\bar{s}]}_{qr}$.

C. Closed-shell cation

Here we used the following four-point, four-times inelastic Green's function in our direct approach:

$$\begin{aligned} iR_{pqrs}(t_f,t,t',t_i) &= -< 0^+|\hat{T}\left[c_p(t_f)c_q(t)c^\dagger_r(t')c^\dagger_s(t_i)\right]|0^+> \\ &\quad + < 0^+|\hat{T}\left[c_p(t_f)c^\dagger_s(t_i)\right]|0^+>< 0^+|\hat{T}\left[c_q(t)c^\dagger_r(t')\right]|0^+> . \end{aligned} \tag{17}$$

$|0^+>$ is the ground state of the cation here, the other parts of the notation are as in the preceding sections.

The spectral representations of the two interesting components in this case are

$$R^{(I)}_{pqrs}(\omega_f,\omega_i,\omega) = \sum_{M,N} \frac{y_p^{[M]\dagger}}{\omega_f-(E^{[M]}-E^{[0^+]})+i0^+}\frac{y_s^{[N]}}{\omega_i-(E^{[N]}-E^{[0^+]})+i0^+} \cdot\left[G^{+[M,N]}_{qr}(\omega)-\delta_{MN}G^{+[0^+,0^+]}_{qr}(\omega-(E^{[M]}-E^{[0^+]})\right]. \quad (18)$$

and

$$R^{(II)}_{pqrs}(\omega'_f,\omega'_i,\omega) = \sum_{M,N} \frac{y_p^{[M]\dagger}}{\omega'_f-(E^{[M]}-E^{[0^+]})+i0^+}\frac{y_s^{[N]}}{\omega'_i-(E^{[N]}-E^{[0^+]})+i0^+} \cdot\left[G^{-[M,N]}_{qr}(\omega)-\delta_{MN}G^{-[0^+,0^+]}_{qr}(\omega-(E^{[M]}-E^{[0^+]})\right], \quad (19)$$

with the transition amplitudes

$$y_s^{[N]} =< N|c_s^\dagger|0^+> . \quad (20)$$

The necessary matrix notation is here

$$R^{(I)}_{pqrs}(\omega_f,\omega_i,\omega) = \mathbf{Y}^\dagger_p \frac{1}{\omega_f-\mathbf{E}-\mathbf{V}}\mathbf{G}_{qr}(\omega)\frac{1}{\omega_i-\mathbf{E}-\mathbf{V}}\mathbf{Y}_s, \quad (21)$$

and an analogous expression for $R^{(II)}$. For the inelastic propagator for $1p$-excitations, only

$$\begin{aligned} R^{(I)(n)}_{pqrs}(\omega_f,\omega_i,\omega) &= \mathbf{Y}^{[1](0)\dagger}_p \frac{1}{\omega_f-\mathbf{E}^{[1]}}\mathbf{G}^{[1,1](n)}_{qr}(\omega)\frac{1}{\omega_i-\mathbf{E}^{[1]}}\mathbf{Y}^{[1](0)}_s+\ldots \quad (22)\\ &= \frac{\bar{n}_p\left(G^{+[p,s](n)}_{qr}(\omega)-\delta_{ps}G^{+[0^+,0^+](n)}_{qr}(\omega-E^{[p]}+E^{[0^+]})\right)\bar{n}_s}{(\omega_f-\epsilon_p+i0^+)(\omega_i-\epsilon_s+i0^+)}\\ &\quad +\ldots \end{aligned}$$

has to be considered, leading again to a reduction in the number of Goldstone diagrams one has to consider for a given Feynman diagram. Here, $G^{+[p,s]}_{qr}$ is the particle component of the inelastic propagator between excitations which are on the Hartree-Fock level simply the states with a particle in orbital p or in orbital s, respectively.

As pointed out in [18], the number of diagrams is here the same as for the case of a closed-shell anion. We will see in the next section that the diagrammatic method for obtaining the inelastic propagator is very similar in these two cases.

III. OBTAINING THE INELASTIC PROPAGATOR DIRECTLY

A. Closed-shell anion

In contrast to the discussion in [18], we present here the case of a closed-shell anion first, since it is easier to treat and therefore more transparent than the case of the closed-shell

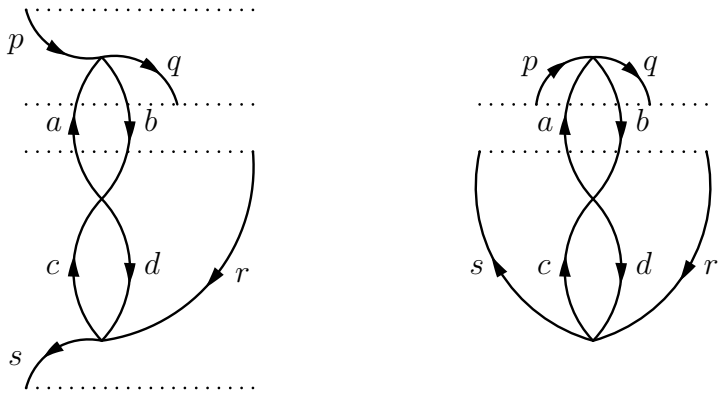

FIG. 1: Example for the limiting procedure in a diagram for the four-point, four-times elastic Green's function for the case of a closed-shell anion. Left: original diagram; right: diagram after the limits were performed.

molecule.

As pointed out in section II B, for calculating the particle component of the inelastic propagator for $1h$-excitations it suffices to look at the diagrams for $R^{(I)}$ where all internal vertices are between t_i and t_f. Unfortunately, even those diagrams do not only give contributions of the general structure shown in (16) directly. We will see that partial fraction decompositions of the expressions resulting from the evaluation of these diagrams are necessary in order to extract the term of the desired structure, and consequently the inelastic Green's function.

Let us start with a simple example. The diagram shown on the left of Fig.1 gives a product of the following terms

$$\frac{n_p}{\omega_f+\epsilon_p+i0^+}\frac{\bar{n}_a n_b n_q}{\omega_f-\epsilon_a+\epsilon_b+\epsilon_q+i0^+}$$
$$\frac{\bar{n}_a n_b}{\omega-\epsilon_a+\epsilon_b+i0^+}$$
$$\frac{\bar{n}_a n_b n_r}{\omega_i-\epsilon_a+\epsilon_b+\epsilon_r+i0^+}\frac{\bar{n}_c n_d n_r}{\omega_i-\epsilon_c+\epsilon_d+\epsilon_r+i0^+}\frac{n_s}{\omega_i+\epsilon_s+i0^+},$$

where the overall sign, permutation factors and interaction factors V are omitted for transparency. By performing partial fraction decompositions in the first and third line, this product can be rewritten to give

$$\frac{n_p}{\omega_f+\epsilon_p+i0^+}\frac{\bar{n}_a n_b n_q}{-\epsilon_a+\epsilon_b+\epsilon_q-\epsilon_p}$$

$$\frac{\bar{n}_a n_b}{\omega - \epsilon_a + \epsilon_b + i0^+}$$
$$\frac{\bar{n}_a n_b n_r}{-\epsilon_a + \epsilon_b + \epsilon_r - \epsilon_s} \frac{\bar{n}_c n_d n_r}{-\epsilon_c + \epsilon_d + \epsilon_r - \epsilon_s} \frac{n_s}{\omega_i + \epsilon_s + i0^+}$$
$$+ \ldots,$$

where the dots denote all the irrelevant terms resulting from the partial fraction decompositions, i. e., terms which are not of the general structure shown in eq. (16).

The rewritten expression differs from the original one given above in that there are only two denominators left which contain the energy variables ω_f and ω_i and the corresponding single-particle energies ϵ_p and ϵ_s. By comparison with eq. (16), we can read off this expression the contribution to the inelastic propagator.

The contribution of this graph for the higher-order Green's function R to the particle component of the inelastic propagator reads then

$$\frac{\bar{n}_a n_b n_q}{-\epsilon_a + \epsilon_b + \epsilon_q - \epsilon_p} \frac{\bar{n}_a n_b}{\omega - \epsilon_a + \epsilon_b + i0^+} \frac{\bar{n}_a n_b n_r}{-\epsilon_a + \epsilon_b + \epsilon_r - \epsilon_s} \frac{\bar{n}_c n_d n_r}{-\epsilon_c + \epsilon_d + \epsilon_r - \epsilon_s}$$

The crucial point is now that this result is the same as the one which would have been obtained by evaluating the right Goldstone diagram shown in Fig.1, with the sole exception that the lines p and s give factors n_p and n_s, respectively, although they are particle lines in the new diagram.

In other words, the above result can be derived directly by deforming the diagram for the higher-order Green's function shown on the left of Fig.1 to obtain the new diagram depicted on the right hand side of that figure. That new diagram gives the desired contribution to the inelastic propagator.

This deformation is achieved by taking the limits $t_f \to t$ and $t_i \to t'$, i. e., by moving the uppermost dotted line downwards and the lowermost dotted line upwards, dragging the vertices p and s and the lines connected to them along. Notice that the auxiliary lines mentioned in the Feynman rules (see [18]), connecting the times (t_f, t) and (t', t_i) vanish when performing these limits.

It will be proven in the appendix that this argument can be generalized: the contribution of a given diagram in the perturbative expansion of $R^{(I)}$ to the particle component of the inelastic propagator can be obtained by taking the limits $t_f \to t$ and $t_i \to t'$, as described above. This will result in there being no lines left after the time of the latest and before the time of the earliest internal vertex. Additionally, between these times and the time t or t',

respectively, there will now be lines for p and s which go upwards, i. e., particle lines instead of the previous hole lines (compare Fig.1). Nevertheless, these two particle lines still have factors n_p and n_s, respectively, associated with them.

Notice that the diagrams obtained in this way correspond to the first component (i. e., for which $t > t'$) of the following Green's function

$$\begin{aligned} iR_{pqrs}(t,t') \;=\; & - < 0^- | \hat{T} \left[c_p^\dagger(t) c_q(t) c_r^\dagger(t') c_s(t') \right] | 0^- > \\ & + < 0^- | \hat{T} \left[c_p^\dagger(t) c_s(t') \right] | 0^- >< 0^- | \hat{T} \left[c_q(t) c_r^\dagger(t') \right] | 0^- >, \end{aligned} \tag{23}$$

which is obtained from (11) by performing the limits $t_f \to t$ and $t_i \to t'$. This Green's function is quite similar to the polarization propagator [19], with the only difference that a different type of disjoint diagrams is subtracted. However, the rules for evaluating the diagrams corresponding to this Green's function are *not* entirely identical to the usual ones.

Using the standard diagrammatic rules, the first component of the Green's function (23) would give the contributions to

$$\sum_{N,M} x_p^{[M]\dagger} \left[G_{qr}^{+[M,N]}(\omega) - \delta_{MN} G_{qr}^{+[0-,0-]} \left(\omega - (E^{[M]} - E^{[0-]}) \right) \right] x_s^{[N]}.$$

It is unclear how one would extract from this result the desired inelastic propagator between the simplest excitations. Even if the transition amplitudes $x_s^{[N]}$ are already known, that would pose a non-trivial problem. On the other hand, using the slightly changed diagrammatic rules we present below (and in more detail in the appendix), this inelastic propagator is directly obtained.

At first sight, only a quite small change is required to the usual diagrammatic evaluation rules: the lines p and s always give factors n_p and n_s, respectively, no matter if they run upwards or downwards. The overall sign of the diagram, factors V and permutation factors are determined exactly as prescribed in the original rules (see [18] and the appendix).

But due to the special rules for occupation number factors for the p and s lines, there are now cases in which the standard evaluation rules do not work properly: diagrams which—before performing the limits—were one-hole-reducible (1HR) in the parts before t' or after t, i. e., diagrams which could be divided into two unconnected parts by cutting one hole line in these time regions. For example, if such a hole line appears after the time t and has the label q (see Fig.2), then (among others) the following factors emerge from the evaluation

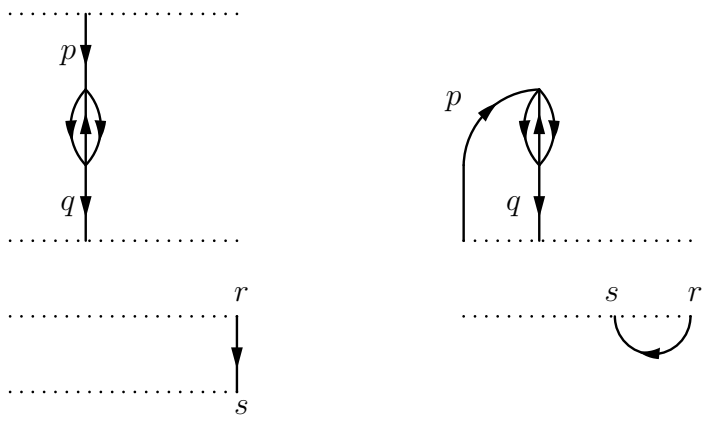

FIG. 2: Example for a diagram for the four-point, four-times elastic Green's function for the case of a closed-shell anion which is one-hole reducible in the part after time t and therefore poses problems (for details, see text). Left: original diagram; right: diagram after the limits were performed.

rules for the cuts:

$$\frac{n_p}{\omega_f + \epsilon_p + i0^+} \frac{n_q}{\omega_f + \epsilon_q + i0^+}$$

A partial fraction decomposition of that expression would result in a contribution to the inelastic propagator containing the factor

$$\frac{n_p n_q}{\epsilon_q - \epsilon_p},$$

which is the same result as one would obtain by evaluating the cuts on the right hand side of Fig.2. Since p also labels a hole state, the two energies in the denominator can be equal, and hence a zero denominator can occur. To handle this, one has to write

$$\frac{n_p}{\omega_f + \epsilon_p + i0^+} \frac{n_q}{\omega_f + \epsilon_q + i0^+} = (\delta_{pq} + \bar{\delta}_{pq}) \frac{n_p}{\omega_f + \epsilon_p + i0^+} \frac{n_q}{\omega_f + \epsilon_q + i0^+}$$

with

$$\bar{\delta}_{pq} = 1 - \delta_{pq}$$

and consider the term with $p = q$ separately, employing again a partial fraction decomposition. (N.B.: We neglect here the possibility of degeneracies, i. e., $\epsilon_p = \epsilon_q$ for $p \neq q$; in principle, such cases could be handled by methods similar to the ones presented below.) This is discussed in detail in the appendix.

It turns out that the rules to evaluate the diagrams which contribute directly to the inelastic propagator have to be amended in the following way:

- The result of the evaluation of the part of the diagram after the time t is a sum of several terms, where the first term is the result of the usual evaluation of the cuts, with extra factors $\bar{\delta}$ in the numerator for every term in the denominator which could be zero.

- Additional terms appear now for every possible combination of the factors δ and $\bar{\delta}$:

  - Every such term has an additional sign factor equal to minus one to the power of the number of factors δ.

  - Every such term consists of the sum of all fractions where the energy factors in the denominator corresponding to the factors δ in the numerator are omitted. Instead, one has to consider all possible combinations of the remaining energy factors, so that the total number of energy factors (counting every power of a factor separately) stays the same in every denominator.

Analogous rules apply to the evaluation of the part of the diagram before the time t'. A proof and a more formal statement of the rules are given in the appendix.

For example, the usual evaluation of the cuts in the left diagram shown in Fig.3 would give

$$\frac{n_p n_a \bar{n}_b n_c n_d}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_d - \epsilon_p)}$$

for the part after time t and

$$\frac{n_s n_f \bar{n}_g n_h n_e}{(\epsilon_f - \epsilon_g + \epsilon_h - \epsilon_s)(\epsilon_e - \epsilon_s)}$$

for the part before time t'. Since the factors $\epsilon_d - \epsilon_p$ and $\epsilon_e - \epsilon_s$ could be zero, these expressions have to be replaced by

$$n_p n_a \bar{n}_b n_c n_d \left(\frac{\bar{\delta}_{dp}}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_d - \epsilon_p)} - \frac{\delta_{dp}}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)^2} \right)$$

and

$$n_s n_e n_f \bar{n}_g n_h \left(\frac{\bar{\delta}_{es}}{(\epsilon_f - \epsilon_g + \epsilon_h - \epsilon_s)(\epsilon_e - \epsilon_s)} - \frac{\delta_{es}}{(\epsilon_f - \epsilon_g + \epsilon_h - \epsilon_s)^2} \right),$$

i. e., we have now sums in which the first term is the result of the direct evaluation of the cuts, amended with a factor $\bar{\delta}$, and one additional term for the case $d = p$ or $e = s$, respectively, appears. In that term, the factor $\epsilon_d - \epsilon_p$ or $\epsilon_e - \epsilon_s$, respectively, is left out in the denominator. Because the total number of energy factors has to remain the same, we therefore need the

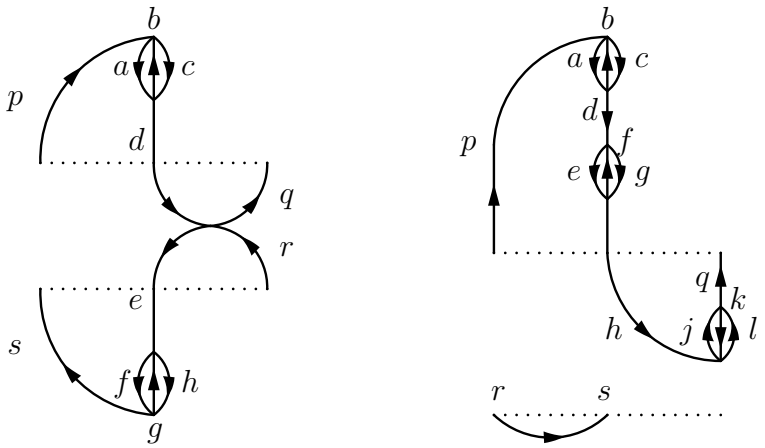

FIG. 3: Two examples for diagrams for the inelastic propagator between $1h$-excitations which pose problems because they have 1HR parts (for details, see text).

second power of the remaining energy factor $\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p$ or $\epsilon_f - \epsilon_g + \epsilon_h - \epsilon_s$, respectively. The sign of this additional term is negative, since one factor δ appears in it.

The evaluation of the diagram hence results in the contribution

$$n_p n_a \bar{n}_b n_c \left(\frac{\bar{\delta}_{dp}}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_d - \epsilon_p)} - \frac{\delta_{dp}}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)^2} \right)$$
$$\frac{n_d \bar{n}_q n_e \bar{n}_r}{\omega + \epsilon_d - \epsilon_q + \epsilon_e - \epsilon_r i0^+}$$
$$n_s n_f \bar{n}_g n_h \left(\frac{\bar{\delta}_{es}}{(\epsilon_f - \epsilon_g + \epsilon_h - \epsilon_s)(\epsilon_e - \epsilon_s)} - \frac{\delta_{es}}{(\epsilon_f - \epsilon_g + \epsilon_h - \epsilon_s)^2} \right)$$

to the particle component of the inelastic propagator.

In contrast, no problems arise with the part of the diagram on the right hand side of Fig.3 which belongs to times before the time t'. It simply gives a factor $n_s \delta_{rs}$, arising from the line connecting the vertices r and s. But the evaluation of the part after time t would give

$$\frac{n_p n_a \bar{n}_b n_c n_d n_e \bar{n}_f n_g n_h}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_d - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)(\epsilon_h - \epsilon_p)}.$$

Both factors $\epsilon_d - \epsilon_p$ and $\epsilon_h - \epsilon_p$ could become zero. Hence we have to treat the four cases $(p \neq d, p \neq h)$, $(p = d, p \neq h)$, $(p \neq d, p = h)$, and $(p = d = h)$ separately. The first case gives the same denominator as the naive evaluation, in the second, the factor $\epsilon_d - \epsilon_p$ is left out, in the third, the factor $\epsilon_h - \epsilon_p$, and in the fourth, both factors. In all four cases, we have then to consider all possible combinations and powers of the remaining energy factors which leave the total number of energy factors the same. This results finally in the following

contribution to the inelastic propagator:

$$
\begin{aligned}
& n_p n_a \bar{n}_b n_c n_d n_e \bar{n}_f n_g n_h \left(\frac{\bar{\delta}_{pd}\bar{\delta}_{ph}}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_d - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)(\epsilon_h - \epsilon_p)} \right. \\
& -\delta_{pd}\bar{\delta}_{ph} \left[\frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)^2(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)(\epsilon_h - \epsilon_p)} \right. \\
& + \frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)^2(\epsilon_h - \epsilon_p)} \\
& \left. + \frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)(\epsilon_h - \epsilon_p)^2} \right] \\
& -\bar{\delta}_{pd}\delta_{ph} \left[\frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)^2(\epsilon_d - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)} \right. \\
& + \frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_q - \epsilon_p)^2(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)} \\
& \left. + \frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_q - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)^2} \right] \\
& +\delta_{pd}\delta_{ph} \left[\frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)^3(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)} \right. \\
& + \frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)^2(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)^2} \\
& \left. \left. + \frac{1}{(\epsilon_a - \epsilon_b + \epsilon_c - \epsilon_p)(\epsilon_e - \epsilon_f + \epsilon_g - \epsilon_p)^3} \right] \right) \\
\times \; & \frac{n_h \bar{n}_q}{\omega + \epsilon_h - \epsilon_q + i0^+} \frac{n_h \bar{n}_j n_k \bar{n}_l}{\omega + \epsilon_h - \epsilon_j + \epsilon_k - \epsilon_l + i0^+} \frac{1}{\omega + i0^+} n_s \delta_{rs}
\end{aligned}
$$

Summarizing, the particle component of the inelastic Green's function can be evaluated diagrammatically in the following way:

1. Draw and evaluate all diagrams for the Green's function (23) according to the usual Feynman rules (see e. g. [18]). The single exception is that the lines with indices p and s contribute always a factor n_p or n_s, respectively, no matter if they run up- or downwards.

2. If the diagram is one-hole-reducible in the parts before time t or after time t', replace the results of the corresponding cuts with sums containing factors δ and $\bar{\delta}$, as outlined above.

The detailed rules for drawing and evaluating the diagrams are provided in the appendix.

Finally, look at the spectral representation for the second component of the higher-order elastic Green's function, given in (13). It is obvious that the only difference in the general

structure is that the energy variables ω'_f and ω'_i appear there instead of the usual ω_f and ω_i. This corresponds in the diagrams to a different ordering of the dotted lines: The second line counting from below corresponds to the time t, and the third to the time t'. For extracting the hole component of the inelastic propagator, we can then use arguments very similar to those employed above for the component $R^{(I)}$.

We conclude that when one draws the Goldstone diagrams for $R^{(II)}$, performs the limits $t_i \to t$ and $t_f \to t'$, and then evaluates the resulting diagrams according to the rules given above (paying special attention to the reducible diagrams), one obtains the contributions to the hole component of the inelastic propagator. This argument is explained in more detail, and proved, in the appendix.

B. Closed-shell cation

This case is very similar to the one discussed in the preceding section. We again look at only the diagrams for $R^{(I)}$ where all internal vertices are between t_i and t_f. Here we are interested in diagrams which give terms of the general structure shown in (22). That is, from a general expression resulting from the evaluation of a Goldstone diagram, we have to extract the contribution which has exactly one factor

$$\frac{\bar{n}_p}{\omega - \epsilon_p + i0^+}$$

and exactly one factor

$$\frac{\bar{n}_s}{\omega - \epsilon_s + i0^+},$$

using partial fraction decompositions.

It turns out that we can get the contributions to the particle component of the inelastic propagator resulting from these decompositions by evaluating instead a diagram where the limits $t_f \to t$ and $t_i \to t'$ were performed, as described previously. For the evaluation of the resulting diagram, the usual diagrammatic rules can be used, with the sole exception that the lines p and s always give factor $\bar{n}_p$ and $\bar{n}_s$, respectively, no matter if they run up– or downwards.

The resulting diagrams correspond to the first component of the Green's function

$$\begin{aligned} iR_{pqrs}(t,t') \;=\; & - < 0^+ | \hat{T} \left[c_p(t) c_q(t) c_r^\dagger(t') c_s^\dagger(t') \right] | 0^+ > \\ & + < 0^+ | \hat{T} \left[c_p(t) c_s^\dagger(t') \right] | 0^+ >< 0^+ | \hat{T} \left[c_q(t) c_r^\dagger(t') \right] | 0^+ >, \end{aligned} \tag{24}$$

which is obtained from (17) by performing the limits $t_f \to t$ and $t_i \to t'$. Similar arguments as in the case of the closed-shell anion apply here also. Especially, note that using the standard diagrammatic rules, the first component of the Green's function (24) would give the contributions to

$$\sum_{N,M} y_p^{[M]\dagger} \left[G_{qr}^{+[M,N]}(\omega - \delta_{MN} G_{qr}^{+[0+,0+]}(\omega - (E^{[M]} - E^{[0+]}) \right] y_s^{[N]},$$

for which it is unclear how one could extract the desired inelastic propagator between the simplest excitations. Again, by employing the slightly changed diagrammatic rules we describe here, this inelastic propagator is directly obtained.

Diagrams which are one-particle-reducible (1PR) in the parts before t' or after t, i. e., diagrams which can be divided into two unconnected parts by cutting one particle line in these time regions (before the limits were performed), pose a problem here. This problem can be dealt with in a way analogous to the case of the anion: introduce factors δ and $\bar{\delta}$ and evaluate the different contributions separately. The resulting rules are the same as previously (see section III A).

Again, the hole component of the inelastic propagator can be obtained from the component $R^{(II)}$ of the original higher-order Green's function, using the same methods. A more formal statement and proof of the diagrammatic rules for evaluating both components of the inelastic propagator for a closed-shell cation can be found in the appendix.

C. Closed-shell neutral molecule

Here only diagrams for $R^{(I)}$ which give terms of the general structure shown in (8) are relevant for the inelastic propagator. Such terms can only come from diagrams which have internal vertices only at times between t_i and t_f. From the results of the evaluations of such diagrams, we have then to extract the contributions which have exactly one factor

$$\frac{n_p \bar{n}_q}{\omega + \epsilon_p - \epsilon_q + i0^+}$$

and exactly one factor

$$\frac{\bar{n}_t n_u}{\omega - \epsilon_t + \epsilon_u + i0^+},$$

using partial fraction decompositions.

Again, we can get the contributions of these diagrams to the particle component of the inelastic propagator by performing the limits $t_f \to t$ and $t_i \to t'$, i. e., moving the uppermost dotted line downwards and the lowermost dotted line upwards, carrying the external vertices p, q, t and u along. Fig.4 shows three illustrative examples. On the left side, the original diagrams for $R^{(I)}$ are shown, on the right side the resulting diagrams after the limits are performed.

The resulting diagrams are evaluated using the usual diagrammatic rules, with the exception that the lines p and u always give occupation number factors n_p and n_u, respectively, and the lines q and t always give factors $\bar{n}_q$ and $\bar{n}_t$, no matter of the direction in which they are running.

These diagrams correspond to the first component of the Green's function

$$\begin{aligned} & iR_{pqrstu}(t,t') \qquad (25) \\ = & - < 0|\hat{T}\left[c_p^\dagger(t)c_q(t)c_r(t)c_s^\dagger(t')c_t^\dagger(t')c_u(t')\right]|0> \\ & + < 0|\hat{T}\left[c_p^\dagger(t)c_q(t)c_r(t)c_s^\dagger(t')\right]|0>< 0|c_t^\dagger(t')c_u(t')|0> \\ & + < 0|\hat{T}\left[c_r(t)c_s^\dagger(t')c_t^\dagger(t')c_u(t')\right]|0>< 0|c_p^\dagger(t)c_q(t)|0> \\ & + < 0|\hat{T}\left[c_p^\dagger(t)c_q(t)c_t^\dagger(t')c_u(t')\right]|0>< 0|\hat{T}\left[c_r(t)c_s^\dagger(t')\right]|0> \\ & -2 < 0|c_p^\dagger(t)c_q(t)|0>< 0|\hat{T}\left[c_r(t)c_s^\dagger(t')\right]|0>< 0|c_t^\dagger(t')c_u(t')|0>, \end{aligned}$$

which results from (3) when the limits $t_f \to t$ and $t_i \to t'$ are considered. It is essentially a $2p1h$-propagator with some disjoined diagrams subtracted. By applying the usual diagrammatic rules, the first component of the Green's function (25) would give

$$\sum_{M\neq 0, N\neq 0} \rho_{pq}^{[0,M]} \cdot \left[G_{rs}^{+[M,N]}(\omega) - \delta_{MN} G_{rs}^{+[0,0]}(\omega - (E^{[M]} - E^{[0]}))\right] \rho_{tu}^{[N,0]},$$

which receives various contributions from inelastic propagators between different types of excitations. In contrast, the diagrammatic rules which we present here give the inelastic propagator between the simplest excitations directly.

Here we have problems with three types of reducible diagrams: those which are one-particle-, one-hole- or one-particle-one-hole-reducible (1P1HR) in the parts before t' or after t, i. e., diagrams which can be divided into two unconnected parts by cutting one particle line or one hole line or both in these time regions (before the limits were performed). For remedying this, we have to introduce appropriate factors δ and $\bar{\delta}$; here the abbreviations

$$\delta_{pq,rs} = \delta_{pr}\delta_{qs}$$

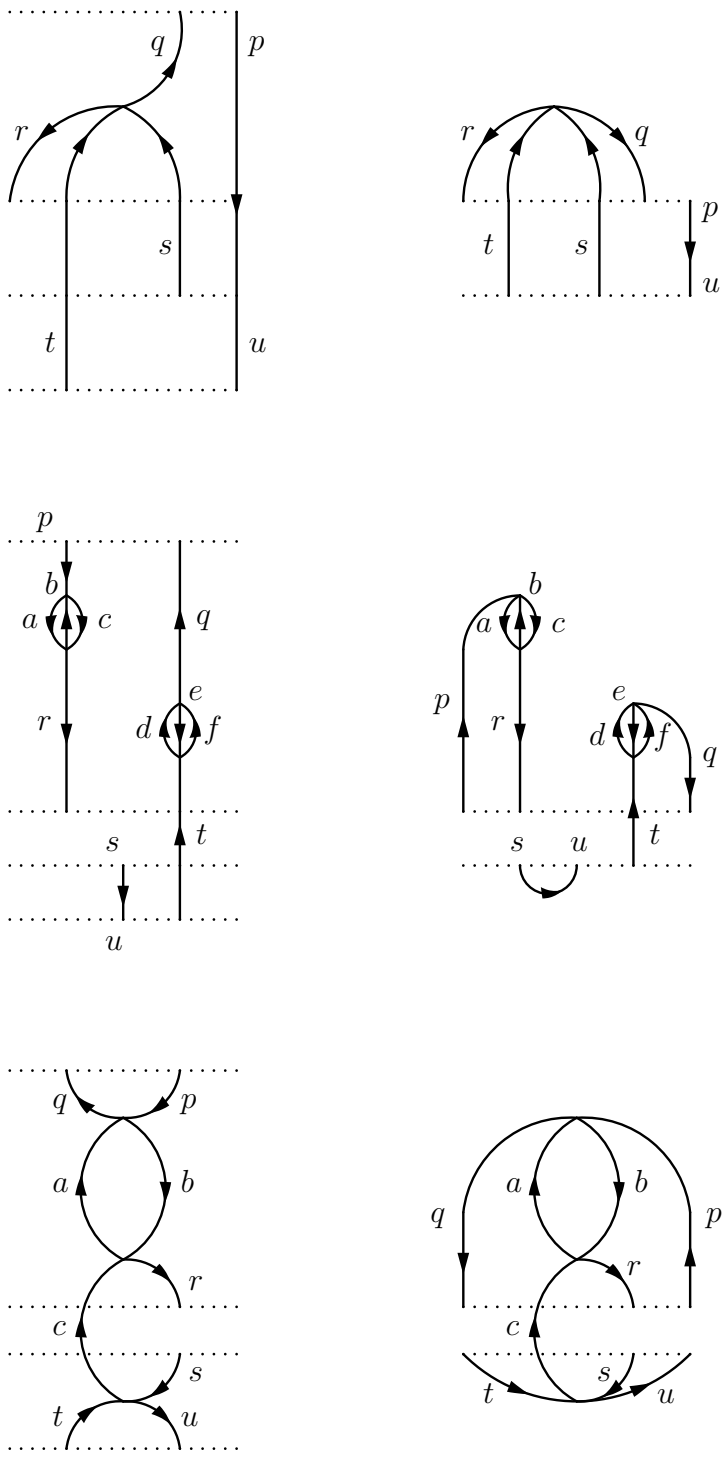

FIG. 4: Three examples for the limiting procedure in diagrams for the six-point, four-times elastic Green's function for the case of a closed-shell neutral molecule. Left: original diagrams; right: diagrams after the limits were performed.

and

$$\bar{\delta}_{pq,rs} = 1 - \delta_{pq,rs}$$

are useful. A closer analysis reveals that we have the same rules as previously (see section III A) then.

As an example, consider what one gets by evaluating the middle diagram on the right side of Fig.4:

$$\frac{n_p n_a \bar{n}_b n_c n_r \bar{n}_d n_e \bar{n}_f \bar{n}_q \bar{n}_t n_u \delta_{su}}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_r)(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)(-\epsilon_p + \epsilon_r - \epsilon_t + \epsilon_q)} \times \frac{1}{\omega - \epsilon_t + i0^+}$$

The second and the fourth factor in the denominator of the first fraction could become zero. Hence we have to introduce appropriate factors δ and $\bar{\delta}$ and replace this single fraction with a sum over fractions. In these fractions, the energy factors in the denominators corresponding to the factors δ in the numerators are left out, and the remaining factors have to be combined in all possible ways so that the total number of energy factors remains the same. The final result is then:

$$\begin{aligned}
&\Bigg(\frac{\bar{\delta}_{rp}\bar{\delta}_{rt,pq}}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_r)(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)(-\epsilon_p + \epsilon_r - \epsilon_t + \epsilon_q)} \\
&-\delta_{rp}\bar{\delta}_{rt,pq}\left[\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)^2(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)(-\epsilon_p + \epsilon_r - \epsilon_t + \epsilon_q)} \right. \\
&+\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)^2(-\epsilon_p + \epsilon_r - \epsilon_t + \epsilon_q)} \\
&\left.+\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)(-\epsilon_p + \epsilon_r - \epsilon_t + \epsilon_q)^2} \right] \\
&-\bar{\delta}_{rp}\delta_{rt,pq}\left[\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)^2(-\epsilon_p + \epsilon_r)(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)} \right. \\
&+\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_r)^2(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)} \\
&\left.+\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_r)(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)^2} \right] \\
&+\delta_{rp}\delta_{rt,pq}\left[\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)^3(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)} \right. \\
&+\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)^2(-\epsilon_p + \epsilon_r - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)^2} \\
&\left.+\frac{1}{(-\epsilon_p + \epsilon_a - \epsilon_b + \epsilon_c)(-\epsilon_p + \epsilon_g - \epsilon_d + \epsilon_e - \epsilon_f + \epsilon_q)^3} \right] \Bigg)
\end{aligned}$$

$$\times \frac{n_p n_a \bar{n}_b n_c n_r \bar{n}_d n_e \bar{n}_f \bar{n}_q \bar{n}_t n_u \delta_{su}}{\omega - \epsilon_t + i0^+}$$

In contrast to the ionic cases, it can here happen that there are no additional energy factors which could replace the left-out energy factors in the additional summands. In such a case, the corresponding summand is simply left out. An example for this is provided by the diagram shown in the lower right of Fig.4, where a naive evaluation would give a contribution to the inelastic propagator containing the fractions

$$\frac{n_p \bar{n}_a n_b \bar{n}_q \bar{n}_c n_r n_s \bar{n}_t n_u}{(-\epsilon_a + \epsilon_b + \epsilon_q - \epsilon_p)(-\epsilon_c + \epsilon_r + \epsilon_q - \epsilon_p)} \frac{1}{\omega - \epsilon_c + i0^+} \frac{1}{-\epsilon_c + \epsilon_s + \epsilon_t - \epsilon_u}$$

The denominators of the first and the last fraction could become zero, hence we have to replace them with sums of fractions which have appropriate factors δ and $\bar{\delta}$ in the numerators, and leave out the corresponding factors in the denominators. The remaining factors have to be combined in a way so that the total number of energy factors remains the same. Obviously, in the cases that in the first fraction both factors are left out, or that in the last fraction the only appearing factor is left out, nothing is left to compensate for the left-out factors—and hence no corresponding fractions can appear in the sums. The final result is thus:

$$\begin{aligned}
&\left[\frac{\bar{\delta}_{ab,qp} \bar{\delta}_{cr,qp}}{(-\epsilon_a + \epsilon_b + \epsilon_q - \epsilon_p)(-\epsilon_c + \epsilon_r + \epsilon_q - \epsilon_p)} - \frac{\delta_{ab,qp} \bar{\delta}_{cr,qp}}{(-\epsilon_c + \epsilon_r + \epsilon_q - \epsilon_p)^2} \right. \\
&\left. - \frac{\bar{\delta}_{ab,qp} \delta_{cr,qp}}{(-\epsilon_a + \epsilon_b + \epsilon_q - \epsilon_p)^2} \right] \\
\times\ & \frac{1}{\omega - \epsilon_c + i0^+} \\
\times\ & \frac{n_p \bar{n}_a n_b \bar{n}_q \bar{n}_c n_r n_s \bar{n}_t n_u \bar{\delta}_{cs,tu}}{-\epsilon_c + \epsilon_s + \epsilon_t - \epsilon_u}
\end{aligned}$$

Like for the ionic cases, the method works also for obtaining the hole component of the inelastic propagator from the component $R^{(II)}$ of the original higher-order Green's function. The appendix contains also for this case of a neutral closed-shell molecule a more formal statement of the Feynman rules for constructing and evaluating the diagrams for both components of the inelastic propagator, and a proof.

D. Higher excitations

In principle, the methods presented here could also be used to obtain the inelastic propagator between higher excited states. The general construction method would be as follows:

1. Construct an appropriate higher-order elastic Green's function, which contains creation and annihilation operators at the times t' and t which create and destroy, respectively, the desired type of excitation, and additionally a creation operator at time t' and an annihilation operator at time t. This Green's function results from one where the excitations are created at time t_i and destroyed at time t_f by performing the limits $t_i \to t'$ and $t_f \to t$.

2. For obtaining the contribution of order n to the particle component of the natural inelastic propagator between these excitations, draw all Goldstone diagrams for the first component of this Green's function.

3. Evaluate these diagrams with the usual Feynman rules for obtaining permutation factors, factors V for the vertices, factors δ for the free Green's function lines, energy denominators, and occupation number factors. The lines corresponding to the excitations always give occupation number factors corresponding to the type of excitation which is created or destroyed, i. e., lines corresponding to a hole created at time t' or destroyed at time t always give a factor n, lines corresponding to a particle always give a factor $\bar{n}$, irrespective of the actual directions of these lines.

4. Pay special attention to diagrams which would have been reducible before taking the limits, i. e., diagrams which give energy denominators which could become zero. Handle these by introducing appropriate factors δ and $\bar{\delta}$, and replacing the result of the naive evaluations with sums over fractions with the problematic energy factors left out and replaced by combinations of the other energy factors, as outlined in the preceding sections.

The hole component of the inelastic propagator can be obtained using analogous rules.

For example, if one wants to have the particle component of the inelastic propagator between $1h$- and $2h1p$-excitations of an ion, one has to employ the six-point, four-times elastic Green's function defined by

$$\begin{aligned} & iR_{pqrstu}(t,t,t',t) \\ = & - < 0^- | \hat{T} \left[c_p^\dagger(t) c_q(t) c_r^\dagger(t') c_s(t') c_t^\dagger(t') c_u(t') \right] | 0^- > \\ & + < 0^- | \hat{T} \left[c_p^\dagger(t) c_s(t') c_t^\dagger(t') c_u(t') \right] | 0^- >< 0^- | \hat{T} \left[c_q(t) c_r^\dagger(t') \right] | 0^- >, \end{aligned}$$

where the operators c_s, $c_t^\dagger$, and c_u create a $2h1p$-excitation at time t' and the operator $c_p^\dagger$ destroys a $1h$-excitation at time t.

The particle component of the inelastic propagators can then be obtained by drawing all Goldstone diagrams with $t > t'$ and obtaining permutation factors, vertex factors, factors δ, occupation numbers and energy denominators for these diagrams according to the usual Feynman rules. The lines p, s, and u give here always factors n_p, n_s, and n_u, respectively, whereas the line t always gives a factor n_t, irrespective of the directions of these lines.

Special attention has to be paid to diagrams where the part after time t is 1HR, or where the part before time t' is reducible (1PR, 1HR, 1P1HR, 2HR, or 2H1PR). One has to introduce factors $\delta_{pp'}$ and $\bar{\delta}_{pp'}$, $\delta_{tt'}$ and $\bar{\delta}_{tt'}$, $\delta_{ss'}$ and $\bar{\delta}_{ss'}$, etc., or $\delta_{stu,s't'u'}$ and $\bar{\delta}_{stu,s't'u'}$ then and replace the results of the naive evaluation with sums over fractions with all different combinations of the δ and $\bar{\delta}$. For every combination, one has to use a sum over fractions where the energy factors corresponding to the factors δ are left out, and all possible combinations of the remaining energy factors appear which leave the total number of energy factors constant.

As a specific example, consider the graph shown on the right side of Fig.5, which results after the limits were performed in the graph shown on the left side. A naive evaluation of the cuts would give here

$$\frac{n_p\bar{n}_q}{\omega+\epsilon_p-\epsilon_q+i0^+}\,\frac{n_sn_rn_u\bar{n}_t\bar{n}_a}{(-\epsilon_s+\epsilon_p-\epsilon_q+\epsilon_r-\epsilon_u+\epsilon_t)(-\epsilon_a+\epsilon_r-\epsilon_u+\epsilon_t)}$$

The two factors in the second fraction could become zero: the first factor for $s = p$, $q = t$, $u = r$ or $s = r$, $q = t$, $u = p$, the second factor for $u = r$, $t = a$. Hence this fraction has to be replaced by a sum of fractions, involving appropriate factors $\delta_{stu,pqr}$, $\bar{\delta}_{stu,pqr}$, $\delta_{ut,ra}$ and $\bar{\delta}_{ut,ra}$, where in the denominators the corresponding energy factor is replaced by all possible combinations of the remaining factors. Note that in the case where both factors are left out, there are no remaining factors to compensate, and hence the corresponding summand simply does not appear—just as described in the case of the simple excitations for the neutral closed-shell molecule in section III C.

IV. SUMMARY AND DISCUSSION

We have developed a method for obtaining the natural inelastic propagator directly by evaluation of diagrams. Our method is based on the 'direct approach' presented in [18].

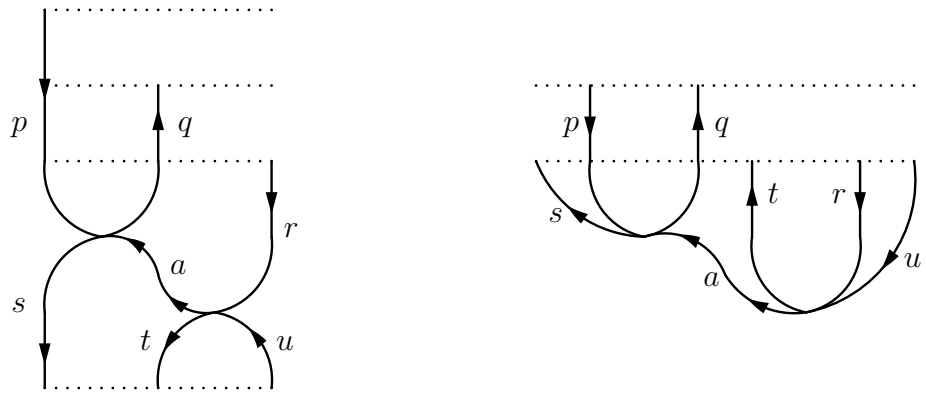

FIG. 5: Example for the limiting procedure in a diagram for the six-point, four-times elastic Green's function for the case of a closed-shell anion. Left: original diagram; right: diagram after the limits were performed.

There, it was shown how one can obtain the inelastic propagator from the spectral representation of a higher-order elastic Green's function. The methods we presented there were plagued by the problem that one had to extract the desired inelastic propagator from the results of a diagrammatic evaluation of the higher Green's function.

In this work, we demonstrated how it is possible to obtain the inelastic propagator for the simplest excitations (i.e. $1h$-, $1p$-, or $1p1h$-excitations, for the case of a closed-shell anion, cation, or neutral target molecule, respectively) directly with diagrammatic methods, without having to evaluate the higher Green's function explicitly. This was achieved by considering that only a certain class of terms from the evaluation of the higher Green's function actually gives contributions to the inelastic propagator, and analyzing how the propagator can be obtained from these terms by doing partial fraction decompositions. It was then shown how the results of these partial fraction decompositions can be obtained directly by slightly changing the usual Feynman rules for the construction and evaluation of the diagrams.

At first it might look like a drawback that the method presented here gives the inelastic propagator for the simplest excitations only, whereas the original 'direct approach' yielded also the propagator for higher excitations. But we showed in section III D how this can be remedied: define higher-order elastic Green's functions for the desired type of excitations, and evaluate these with methods analogous to the ones we presented for the simple

excitations.

Consider further that the new approach has a distinct advantage compared to the previously presented 'direct approach': diagrams corresponding to order n of perturbation theory (i. e., containing n vertices) directly give the contributions of order n to the desired inelastic propagator, whereas in the direct approach, only lower orders were obtained for propagators between higher excitations (e. g., the diagrams of first order for the six-point, four-times elastic Green's function gave only the zeroth order contributions to the inelastic propagator between $1p1h$- and $2p2h$-excitations, see [18]).

Note that in principle the methods we developed here could also be used in the 'Dyson approach' we presented in [18]. That approach employs the evaluation of higher-order elastic Green's functions from whose spectral representation the generalized densities can be obtained. Using Dyson-like equations, it is then possible to calculate the inelastic propagator from these densities.

As in the 'direct approach', the 'Dyson approach' was also plagued by the problem of extracting the desired expressions, here the generalized densities, out of the results of the diagrammatic evaluation of the higher-order Green's function. The methods discussed here could be used to facilitate that extraction: by a diagrammatic evaluation method analogous to that used for the direct approach, involving a limiting procedure, one would obtain the generalized densities directly.

The number of Goldstone diagrams per Feynman diagram one has to consider then in order n of perturbation theory is only $n+1$ (compared to $(n+3)!/3!$ in the original Dyson approach), i. e., one achieves a significant reduction in the number of diagrams. On the other hand, one obtains only the generalized densities for the simplest excitations with this method (i. e. $1h$-, $1p$-, or $1p1h$-excitations, respectively). This could be remedied by a generalization of the method along the lines discussed for the 'direct approach' in section III D.

As already mentioned in [18], the 'Dyson approach' is especially useful for treating the scattering of projectiles which are *distinguishable* from the particles of the target (e. g. positron-molecule scattering), since in these cases the self-energy, which is an optical potential for the scattering, can already be calculated when only the densities are known [15]. In contrast, when the projectile is *indistinguishable* from the particles of the target, the full inelastic Green's function is needed in order to calculate the optical potential.

Then, a problem which was already discussed in [18] arises: for evaluating the Dyson-like equations, not only the generalized densities for the excitations of interested are needed, but also higher excitations. Hence in that case, the Dyson approach generally requires a considerable amount of additional work, compared to the direct approach.

Finally, note that having a diagrammatic evaluation scheme available which gives the inelastic propagator directly is a step forward, but still not sufficient compared to the methods available for the *elastic* one-particle propagator, or the polarization propagator. For the latter ones, approximation schemes like the random-phase approximation [20], the outer-valence Green's function method [21] or the partial third-order approximation [22] had been proposed which not only make use of a perturbative diagrammatic evaluation, but also take some higher-order contributions into account. The Algebraic Diagrammatic Construction scheme [23–25] is a successful attempt to do such partial resummations in a systematic way. It would be very desirable to extend this scheme also to the inelastic propagator.

APPENDIX: DIAGRAMMATIC RULES FOR THE INELASTIC PROPAGATOR AND THEIR PROOF

1. Preliminaries

We will show and prove now how one can get from the Feynman rules for the first and second components $R^{(I)}$ and $R^{(II)}$ of the four-point, four-times elastic Green's function for a closed-shell anion to rules with which one can directly construct and evaluate diagrams for the natural inelastic propagator $G^{[\bar{p},\bar{s}]}$.

A general Goldstone diagram for $R^{(I)}(\omega_f, \omega_i, \omega)$ where t_f is after and t_i is before all internal vertices will give a sum (over internal particle indices) of terms which can be written as

$$f(\omega_f) \times g(\omega) \times h(\omega_i),$$

where the function $g(\omega)$ contains all the factors δ, n, $\bar{n}$, V and all denominators containing ω, and the functions $f(\omega_f)$ and $h(\omega_i)$ are only products of fractions with numerator 1 and denominators containing ω_f or ω_i, respectively. Denominators with combinations of the ω's or without an ω can not result due to the restrictions imposed on the possible time orderings.

For obtaining $G^{+[\bar{p},\bar{s}]}$, we need to extract from this the contributions which look like

$$\frac{1}{\omega_f + \epsilon_p + i0^+} \tilde{g}(\omega) \frac{1}{\omega_i + \epsilon_s + i0^+}.$$

Hence we have to extract the contribution with only one factor

$$\frac{1}{\omega_f + \epsilon_p + i0^+}$$

(and no other ω_f-denominators) from $f(\omega_f)$ and the contribution with only one factor

$$\frac{1}{\omega_i + \epsilon_s + i0^+}$$

(and no other ω_i-denominators) from $h(\omega_i)$. We will show explicitly how to do the first extraction; the second works completely analogously.

The evaluation of the cuts for a diagram for $R^{(I)}$ gives for $f(\omega_f)$ always an expression which can be written as

$$\frac{1}{\omega_f + \epsilon_p + i0^+} \prod_{j=1}^{J} \frac{1}{\omega_f + \epsilon_{q_j} + i0^+} \prod_{m=1}^{M} \frac{1}{\omega_f + E_m + i0^+}, \tag{A.1}$$

where the E_m are sums of particle and hole energies (not simply one hole energy). The first term comes from a cut through the part of the diagram between the latest internal vertex and the time t_f, the other terms come from cuts between vertices at times between t and the latest internal vertex. For obtaining the contribution which has only one factor

$$\frac{1}{\omega_f + \epsilon_p + i0^+}$$

and no other ω_f-denominators, one has to perform partial fraction decompositions of this expression. One encounters then the problem that the q_j can be equal to p, which would lead to zero denominators.

Hence we first write for the 1 in the numerators of the fractions with only the hole energies q_j in the denominators:

$$1 = \delta_{pq_j} + \bar{\delta}_{pq_j}$$

and introduce the notation N_J for the set $\{1, 2, \ldots, N\}$. As usual, the number of elements in the set A in denoted with $\#A$, and the power set of the set N_J with $\mathcal{P}(N_J)$. Then (A.1) can be written as:

$$\sum_{A \in \mathcal{P}(N_J)} \frac{\prod_{j \in A} \delta_{pq_j}}{(\omega_f + \epsilon_p + i0^+)^{\#A+1}} \prod_{j \in N_J \setminus A} \frac{\bar{\delta}_{pq_j}}{\omega_f + \epsilon_{q_j} + i0^+} \prod_{m=1}^{M} \frac{1}{\omega_f + E_m + i0^+} \tag{A.2}$$

If we now further introduce the abbreviations $\tilde{E}_k = E_k$ for all $1 \leq k \leq M$ and $\tilde{E}_{M+k} = \epsilon_{q_{j_k}}$ with $j_k \in N_J \setminus A$ for all $1 \leq k \leq J - \#A$, $j_1 \leq j_2 \leq \ldots \leq j_{J-\#A}$, this can be rewritten as

$$\sum_{A \in \mathcal{P}(N_J)} \frac{\prod\limits_{j \in A} \delta_{pq_j}}{(\omega_f + \epsilon_p + i0^+)^{\#A+1}} \prod_{j \in N_J \setminus A} \bar{\delta}_{pq_j} \prod_{k=1}^{M+J-\#A} \frac{1}{\omega_f + \tilde{E}_k + i0^+} \tag{A.3}$$

Since we only want to have terms with a single factor

$$\frac{1}{\omega_f + \epsilon_p + i0^+},$$

we now have to do partial fraction decompositions for each of the summands in (A.3).

For this, we first have to introduce some further mathematical terms. A *partition* of a non-negative integer N is by definition a set of positive integers whose sum gives N [26]. We call a K-tuple for which the sum of the elements gives N an *ordered partition with K elements* of N. The set of all ordered partitions with K elements of the integer $N + K - 1$ will be denoted by $P(N, K)$, and for $p \in P(N, K)$, p_j means the element number j of the K-tuple p.

We now claim that if $\tilde{E}_k \neq \epsilon_p$ for all k, then for $N, K \geq 1$

$$\begin{aligned} \frac{1}{(\omega_f + \epsilon_p + i0^+)^N} \prod_{k=1}^{K} \frac{1}{\omega_f + \tilde{E}_k + i0^+} \;=\; & \frac{(-1)^{N+1}}{\omega_f + \epsilon_p + i0^+} \sum_{p \in P(N,K)} \prod_{k=1}^{K} \frac{1}{(\tilde{E}_k - \epsilon_p)^{p_k}} \\ & + \text{ other terms} \end{aligned} \tag{A.4}$$

holds, where "other terms" refers to summands in which

$$\frac{1}{(\omega_f + \epsilon_p + i0^+)^j}$$

with $j \neq 1$ appears, but no other ω_f-denominators. Formula (A.4) can be proven by induction for N and K [27].

Now we can use this formula to evaluate the summands in (A.3) further, since each of them is of the form given on the left hand side of (A.4). This yields:

$$\begin{aligned} & \frac{1}{\omega_f + \epsilon_p + i0^+} \prod_{j=1}^{J} \frac{1}{\omega_f + \epsilon_{q_j} + i0^+} \prod_{m=1}^{M} \frac{1}{\omega_f + E_m + i0^+} \\ = & \sum_{A \in \mathcal{P}(N_J)} \frac{(-1)^{\#A} \prod\limits_{j \in A} \delta_{pq_j}}{\omega_f + \epsilon_p + i0^+} \prod_{j \in N_J \setminus A} \bar{\delta}_{pq_j} \sum_{p \in P(\#A+1, M+J-\#A)} \prod_{k=1}^{M+J-\#A} \frac{1}{(\tilde{E}_k - \epsilon_p)^{p_k}} \\ & + \text{ other terms,} \end{aligned}$$

Thus a diagram for $R^{(I)}$ for which the cuts give a factor

$$f(\omega_f) = \frac{1}{\omega_f + \epsilon_p + i0^+} \prod_{j=1}^{J} \frac{1}{\omega_f + \epsilon_{q_j} + i0^+} \prod_{m=1}^{M} \frac{1}{\omega_f + E_m + i0^+}$$

gives a contribution to $G^{+[\bar{p},\bar{s}]}$ containing the factor

$$\sum_{A \in \mathcal{P}(N_J)} (-1)^{\#A} \prod_{j \in A} \delta_{pq_j} \prod_{j \in N_J \setminus A} \bar{\delta}_{pq_j} \sum_{p \in P(\#A+1, M+J-\#A)} \prod_{k=1}^{M+J-\#A} \frac{1}{(\tilde{E}_k - \epsilon_p)^{p_k}} \tag{A.5}$$

On the other hand, first taking the limit $t_f \to t$ in the diagram as described previously and then evaluating the cuts for the resulting diagrams would have yielded a factor

$$\prod_{j=1}^{J} \frac{1}{\epsilon_{q_j} - \epsilon_p} \prod_{m=1}^{M} \frac{1}{E_m - \epsilon_p}. \tag{A.6}$$

The variable ω_f does not appear anymore in any of the fractions since due to the limit $t_f \to t$, the auxiliary line corresponding to that variable has shrunk to zero. The hole line p was dragged down when taking the limit, becoming a particle line, and hence in all denominators, we now have the term $-\epsilon_p$, and the fraction

$$\frac{1}{\omega_f + \epsilon_p + i0^+}$$

has vanished completely.

We have shown now that instead of the simple expression (A.6) for the factor resulting from the cuts after the time t, the more complicated one shown above in (A.5) has to be used. An analogous line of reasoning can be applied to the terms with ω_i, which result from the cuts before the time t'.

On the other hand, as already pointed out in section III A, the result (A.6) can be obtained by evaluating the diagrams for the first component of the Green's function

$$\begin{aligned} iR_{pqrs}(t,t') \;=\; & - < 0^- | \hat{T} \left[c_p^\dagger(t) c_q(t) c_r^\dagger(t') c_s(t') \right] | 0^- > & \text{(A.7)} \\ & + < 0^- | \hat{T} \left[c_p^\dagger(t) c_s(t') \right] | 0^- >< 0^- | \hat{T} \left[c_q(t) c_r^\dagger(t') \right] | 0^- >, & \text{(A.8)} \end{aligned}$$

with the usual Feynman rules. The only exception is that the lines p and s always get a factor n_p and n_s, regardless of their directions. Hence we can get the inelastic propagator by first evaluating the diagrams for this Green's function, leading to expressions like (A.6), and then replacing these with expressions like (A.5). This realization lead to the Feynman rules for the inelastic propagator we will present in the next section.

An analogous line of reasoning can be used for obtaining the hole component of the inelastic Green's function.

2. Formal statement of the Feynman rules for the case of a closed-shell anion

Collecting everything discussed in the previous sections together, we can formulate the following Feynman rules for the evaluation of the Goldstone diagrams for the natural inelastic propagator in order n:

1. Draw all topologically distinct connected diagrams with n interaction (wavy) lines and $2n+2$ directed free Green's function (solid) lines. If the particle component of the inelastic propagator is desired, both at the times t and t', one line has to start and one line has to end. If the hole component is desired, consider the diagrams where two of the lines starts at time t' and two of the lines end at time t.

2. Skip all disjoint graphs.

3. Employ the Abrikosov notation, i.e., replace the wavy interaction lines by interaction points representing the antisymmetrized matrix elements $V_{ab[cd]}$. Multiply each graph by 2^{-P}, where P is the number of permutations of two free Green's function lines leaving the graph topologically unchanged.

4. For a given nth order Feynman diagram, draw all $(n+2)!/2!$ time-ordered diagrams which result from permuting the ordering of the times t,t',t_1,...,t_n. For the particle component, consider only diagrams with $t > t'$, for the hole component, only diagrams with $t' > t$. Introduce an auxiliary line going from t to t'.

5. Label the graphs with one-particle indices. One of the lines starting at t' gets the label r, one of the lines ending at t gets the label q. In the case of the particle component, the line ending at t' gets the label s, the line starting at t is p. In the case of the hole component, the other line starting at time t' gets the labels p, the other line ending at time t the label s. Every directed free Green's function line contributes a factor δ. Every particle line gives a factor $\bar{n}$, every hole line gives a factor n. The sole exceptions are the lines p and s, which always give a factor n_p or n_s, respectively. Sum over all internal indices.

6. The sign for the graphs is $(-1)^{L+M}$, where L is the number of loops and M the number of hole lines. An additional factor of -1 arises if t is connected to t' (look at the Feynman graphs contained in the Abrikosov graph in order to determine this).

7. Each cut (a horizontal line) between two successive vertices (including the external vertices) introduces a denominator of the type

$$\sigma\omega + \epsilon_k + \epsilon_l + \ldots - \epsilon_i - \epsilon_j - \ldots + i0^+.$$

Here each cut line gives a contribution: hole-lines $k, l, \ldots$ contribute the one-particle energies $\epsilon_k, \epsilon_l, \ldots$; particle lines $i, j, \ldots$ contribute the negative energies $-\epsilon_i, -\epsilon_j, \ldots$. The energy variable ω is introduced if the auxiliary line is cut, and has positive ($\sigma = +1$) or negative sign ($\sigma = -1$), according to the downward or upward direction of the auxiliary line. If the auxiliary line is not cut, then ω does not appear in the denominator, i. e., a constant denominator results, in which the imaginary infinitesimal $i0^+$ can be omitted.

8. The resulting expression can always be written as a sum (over internal particle indices) over terms of the form

$$\prod_{j=1}^{J} \frac{1}{\epsilon_{q_j} - \epsilon_p} \prod_{m=1}^{M} \frac{1}{E_m - \epsilon_p} \times g(\omega) \times \prod_{j=1}^{J'} \frac{1}{\epsilon_{r_j} - \epsilon_s} \prod_{m=1}^{M'} \frac{1}{E'_m - \epsilon_s}$$

with a factor $g(\omega)$ which contains all the factors δ, n, $\bar{n}$, V and all denominators containing ω. The factors before and after $g(\omega)$ have then to be replaced, taking into account that the denominators with q_j or r_j could be zero, resulting in the final expression

$$\begin{aligned}
&\sum_{A \in \mathcal{P}(N_J)} (-1)^{\#A} \prod_{j \in A} \delta_{pq_j} \prod_{j \in N_J \setminus A} \bar{\delta}_{pq_j} \sum_{p \in P(\#A+1, M+J-\#A)} \prod_{k=1}^{M+J-\#A} \frac{1}{(\tilde{E}_k - \epsilon_p)^{p_k}} \\
&\times \; g(\omega) \\
&\times \sum_{A \in \mathcal{P}(N_{J'})} (-1)^{\#A} \prod_{j \in A} \delta_{sr_j} \prod_{j \in N_{J'} \setminus A} \bar{\delta}_{sr_j} \sum_{p \in P(\#A+1, M'+J'-\#A)} \prod_{k=1}^{M'+J'-\#A} \frac{1}{(\tilde{E}'_k - \epsilon_s)^{p_k}},
\end{aligned}$$

where

(a) $\tilde{E}_k = E_k$ for all $1 \le k \le M$ and $\tilde{E}_{M+k} = \epsilon_{q_{j_k}}$ with $j_k \in N_J \setminus A$ for all $1 \le k \le J - \#A$, $j_1 \le j_2 \le \ldots \le j_{J-\#A}$

(b) $\tilde{E}'_k = E'_k$ for all $1 \le k \le M'$ and $\tilde{E}'_{M'+k} = \epsilon_{r_{j_k}}$ with $j_k \in N_{J'} \setminus A$ for all $1 \le k \le J' - \#A$, $j_1 \le j_2 \le \ldots \le j_{J'-\#A}$

The rather obscure mathematical expression in rule 8 is identical to what was stated already previously in section III A: The results for the factors beside $g(\omega)$ are both sums of

terms in which all possible combinations of the δ and $\bar{\delta}$ appear. Every such term is again a sum over fractions with 1 in the numerator. In the denominators, the energy factors corresponding to the factors δ are left out and replaced by all possible combinations of the remaining energy factors, so that the total number of energy factors (counting every power separately) stays the same.

The results obtained by drawing and evaluating the Feynman graphs as outlined above are the contributions in order n to

$$G_{qr}^{[\bar{p},\bar{s}]}(\omega) - \delta_{ps} G_{qr}^{[0^-,0^-]}(\omega - E^{[\bar{p}]} + E^{[0^-]}).$$

On the other hand, if one also includes the disjoint diagrams, the results will be the contributions in order n to the quantity

$$G_{qr}^{[\bar{p},\bar{s}]}(\omega)$$

alone.

3. Formal statement of the Feynman rules for the case of a closed-shell cation

This case is very similar to the anionic case discussed in the preceding sections. Instead of (A.1), we now have the general expression

$$\frac{1}{\omega_f - \epsilon_p + i0^+} \prod_{j=1}^{J} \frac{1}{\omega_f - \epsilon_{q_j} + i0^+} \prod_{m=1}^{M} \frac{1}{\omega_f + E_m + i0^+}, \tag{A.9}$$

for the term $f(\omega_f)$, where the E_m are sums of particle and hole energies (not simply one particle energy). Then one introduces factors δ_{pq_j} and $\bar{\delta}_{pq_j}$ and abbreviations $\tilde{E}_k$ analogously to the preceding sections. This results in

$$\sum_{A \in \mathcal{P}(N_J)} \frac{\prod\limits_{j \in A} \delta_{pq_j}}{(\omega_f - \epsilon_p + i0^+)^{\#A+1}} \prod_{j \in N_J \setminus A} \bar{\delta}_{pq_j} \prod_{k=1}^{M+J-\#A} \frac{1}{\omega_f + \tilde{E}_k + i0^+}. \tag{A.10}$$

By using the formula

$$\begin{aligned} \frac{1}{(\omega_f - \epsilon_p + i0^+)^N} \prod_{k=1}^{K} \frac{1}{\omega_f + \tilde{E}_k + i0^+} \;=\; & \frac{(-1)^{N+1}}{\omega_f - \epsilon_p + i0^+} \sum_{p \in P(N,K)} \prod_{k=1}^{K} \frac{1}{(\tilde{E}_k + \epsilon_p)^{p_k}} \\ & + \text{other terms}, \end{aligned} \tag{A.11}$$

which is exactly analogous to (A.4), one can then extract the desired terms with only one factor

$$\frac{1}{\omega_f - \epsilon_p + i0^+}$$

and no other ω_f-denominators. Again, for the factor $g(\omega_i)$ the argument works exactly analogous. Similarly to the preceding case, it can also be shown that one can get in the same way the hole component of the inelastic propagator from the component $R^{(II)}$ of the higher-order elastic Green's function.

The Green's functions we have to use here are

$$\begin{aligned} iR_{pqrs}(t,t') &= - < 0^+|\hat{T}\left[c_p(t)c_q(t)c_r^\dagger(t')c_s^\dagger(t')\right]|0^+> \\ &\quad + < 0^+|\hat{T}\left[c_p(t)c_s^\dagger(t')\right]|0^+>< 0^+|\hat{T}\left[c_q(t)c_r^\dagger(t')\right]|0^+>, \end{aligned} \tag{A.12}$$

if we consider the particle component, or

$$\begin{aligned} iR_{pqrs}(t,t') &= - < 0^+|\hat{T}\left[c_p(t)c_q(t)c_r^\dagger(t')c_s^\dagger(t')\right]|0^+> \\ &\quad + < 0^+|\hat{T}\left[c_p(t)c_s^\dagger(t')\right]|0^+>< 0^+|\hat{T}\left[c_q(t)c_r^\dagger(t')\right]|0^+>, \end{aligned} \tag{A.13}$$

if we look at the hole component. These result from the first and second components of the four-times, four-point Green's function (17) by taking the appropriate limits.

Hence the Feynman rules for the cationic case can be formulated. They are very similar to those formulated for the anionic case (see 2). What has to be changed are the rules 1, 5, 6, and 8, which read now:

1. Draw all topologically distinct connected diagrams with n interaction (wavy) lines and $2n+2$ directed free Green's function (solid) lines. If the particle component of the inelastic propagator is desired, consider the diagrams where two of the lines starts at time t' and two of the lines end at time t. If the hole component is desired, both at the times t and t', one line has to start and one line has to end.

5. Label the graphs with one-particle indices. One of the lines starting at t' gets the label r, one of the lines ending at t gets the label q. In the case of the particle component, the other line starting at time t' gets the labels s, the other line ending at time t the label p. In the case of the hole component, the line ending at t' gets the label p, the line starting at t is s. Every directed free Green's function line contributes a factor δ. Every particle line gives a factor $\bar{n}$, every hole line gives a factor n. The sole exceptions are the lines p and s, which always give a factor $\bar{n}_p$ or $\bar{n}_s$, respectively. Sum over all internal indices.

6. The sign for those graphs is $(-1)^{L+M}$, where L is the number of loops and M the number of hole lines. An additional factor of -1 arises if t is *not* connected to t' (look at the Feynman graphs contained in the Abrikosov graph in order to determine this).

8. The resulting expression can always be written as a sum (over internal particle indices) over terms of the form

$$\prod_{j=1}^{J} \frac{1}{-\epsilon_{q_j} + \epsilon_p} \prod_{m=1}^{M} \frac{1}{E_m + \epsilon_p} \times g(\omega) \times \prod_{j=1}^{J'} \frac{1}{-\epsilon_{r_j} + \epsilon_s} \prod_{m=1}^{M'} \frac{1}{E'_m + \epsilon_s}$$

with a factor $g(\omega)$ which contains all the factors δ, n, $\bar{n}$, V and all denominators containing ω. The factors before and after $g(\omega)$ have then to be replaced, taking into account that the denominators with q_j or r_j could be zero, resulting in the final expression

$$\begin{aligned} &\sum_{A \in \mathcal{P}(N_J)} (-1)^{\#A} \prod_{j \in A} \delta_{pq_j} \prod_{j \in N_J \setminus A} \bar{\delta}_{pq_j} \sum_{p \in P(\#A+1, M+J-\#A)} \prod_{k=1}^{M+J-\#A} \frac{1}{(\tilde{E}_k + \epsilon_p)^{p_k}} \\ &\times \; g(\omega) \\ &\times \sum_{A \in \mathcal{P}(N_{J'})} (-1)^{\#A} \prod_{j \in A} \delta_{sr_j} \prod_{j \in N_{J'} \setminus A} \bar{\delta}_{sr_j} \sum_{p \in P(\#A+1, M'+J'-\#A)} \prod_{k=1}^{M'+J'-\#A} \frac{1}{(\tilde{E}'_k + \epsilon_s)^{p_k}}, \end{aligned}$$

where

(a) $\tilde{E}_k = E_k$ for all $1 \leq k \leq M$ and $\tilde{E}_{M+k} = -\epsilon_{q_{j_k}}$ with $j_k \in N_J \setminus A$ for all $1 \leq k \leq J - \#A$, $j_1 \leq j_2 \leq \ldots \leq j_{J-\#A}$

(b) $\tilde{E}'_k = E'_k$ for all $1 \leq k \leq M'$ and $\tilde{E}'_{M'+k} = -\epsilon_{r_{j_k}}$ with $j_k \in N_{J'} \setminus A$ for all $1 \leq k \leq J' - \#A$, $j_1 \leq j_2 \leq \ldots \leq j_{J'-\#A}$

The results of the evaluation procedure described above provide the contributions in order n to

$$G_{qr}^{[p,s]}(\omega) - \delta_{ps} G_{qr}^{[0^+,0^+]}(\omega - E^{[p]} + E^{[0^+]}).$$

On the other hand, if one also includes the disjoint diagrams, the results will be the contributions in order n to the quantity

$$G_{qr}^{[p,s]}(\omega)$$

alone.

4. Formal statement of the Feynman rules for the case of a closed-shell neutral molecule

Here we encounter some additional difficulties compared to the cases discussed above in 2 and 3. In the term $f(\omega_f)$, we now have not only factors

$$\frac{1}{\omega_f + \epsilon_p - \epsilon_q + i0^+},$$

and

$$\frac{1}{\omega_f + \epsilon_{p_j} - \epsilon_{q_j} + i0^+},$$

and the product

$$\prod_{m=1}^{M} \frac{1}{\omega_f + E_m + i0^+},$$

where the E_m are sums of particle and hole energies (not simply one particle energy plus one hole energy), but in general also factors

$$\frac{1}{\omega_f + \epsilon_p - \epsilon_{q_j} + i0^+},$$

and

$$\frac{1}{\omega_f + \epsilon_{p_j} - \epsilon_q + i0^+}.$$

Also, it can happen here that $M = 0$. Evaluating the diagrams resulting after the limits are performed, we would then have in the denominators *only* energy factors which can be zero, i. e., none of them would be *always* different from zero.

Fortunately, none of these problems is of a mathematical nature—all of them merely pose some additional problems to our notations. For factors which could be zero, we can again introduce δ's and $\bar{\delta}$'s, and all energy factors can again be collected into the collective notation $\tilde{E}_k$. We just have to pay attention to using the appropriate factors: δ_{pp_j}, δ_{qq_j} or δ_{pq,p_jq_k}.

The Green's functions which have to be considered here are

$$\begin{aligned} & iR_{pqrstu}(t,t') \qquad (A.14) \\ = & - < 0|\hat{T}\left[c_p^\dagger(t)c_q(t)c_r(t)c_s^\dagger(t')c_t^\dagger(t')c_u(t')\right]|0> \\ & + < 0|\hat{T}\left[c_p^\dagger(t)c_q(t)c_r(t)c_s^\dagger(t')\right]|0>< 0|c_t^\dagger(t')c_u(t')|0> \\ & + < 0|\hat{T}\left[c_r(t)c_s^\dagger(t')c_t^\dagger(t')c_u(t')\right]|0>< 0|c_p^\dagger(t)c_q(t)|0> \end{aligned}$$

$$
\begin{aligned}
&+ < 0|\hat{T}\left[c_p^\dagger(t)c_q(t)c_t^\dagger(t')c_u(t')\right]|0 >< 0|\hat{T}\left[c_r(t)c_s^\dagger(t')\right]|0 > \\
&-2 < 0|c_p^\dagger(t)c_q(t)|0 >< 0|\hat{T}\left[c_r(t)c_s^\dagger(t')\right]|0 >< 0|c_t^\dagger(t')c_u(t')|0 >,
\end{aligned}
$$

for the particle component and

$$
\begin{aligned}
& iR_{pqrstu}(t,t') \qquad\qquad (A.15)\\
= & - < 0|\hat{T}\left[c_p^\dagger(t')c_q(t')c_s^\dagger(t')c_r(t)c_t^\dagger(t)c_u(t)\right]|0 > \\
& + < 0|\hat{T}\left[c_p^\dagger(t')c_q(t')c_s^\dagger(t')c_r(t)\right]|0 >< 0|c_t^\dagger(t)c_u(t)|0 > \\
& + < 0|\hat{T}\left[c_s^\dagger(t')c_r(t)c_t^\dagger(t)c_u(t)\right]|0 >< 0|c_p^\dagger(t')c_q(t')|0 > \\
& + < 0|\hat{T}\left[c_p^\dagger(t')c_q(t')c_t^\dagger(t)c_u(t)\right]|0 >< 0|\hat{T}\left[c_s^\dagger(t')c_r(t)\right]|0 > \\
& -2 < 0|c_p^\dagger(t')c_q(t')|0 >< 0|\hat{T}\left[c_s^\dagger(t')c_r(t)\right]|0 >< 0|c_t^\dagger(t)c_u(t)|0 >,
\end{aligned}
$$

for the hole component, resulting from taking the appropriate limits of first and second component of the original four-times, six-point Green's function (3).

This enables us to formulate the Feynman rules for the case of a neutral closed-shell molecule. Most rules are identical to those formulated for the cases of the closed-shell ions (see sections 2 and 3). Rules 1, 5, 6, and 8 have to be changed to:

1. Draw all topologically distinct connected diagrams with n interaction (wavy) lines and $2n+3$ directed free Green's function (solid) lines, with two lines starting at time t', one line ending at t', one line starting at t and two lines ending at t.

5. Label the graphs with one-particle indices. One of the lines starting at t' gets the label s, one of the lines ending at t gets the label r. In the case of the particle component, the other line starting at time t' gets the labels t, the other line ending at time t the label q, the line ending at t' is u, and the line starting at t is p. In the case of the hole component, the other line starting at t' gets the label p, the other line ending at t is u, the line ending at t' is q, and the line starting at t is t. Every directed free Green's function line contributes a factor δ. Every particle line gives a factor $\bar{n}$, every hole line gives a factor n. The sole exceptions are the lines p, q, t, and u, which always give a factor n_p, $\bar{n}_q$, $\bar{n}_t$ or n_u, respectively. Sum over all internal indices.

6. The sign for those graphs is $(-1)^{L+M}$, where L is the number of loops and M the number of hole lines. An additional factor of -1 arises for the connections

- p to u, q to t, r to s
- p to r, q to s, t to u
- t to r, u to s, p to q

(look at the Feynman graphs contained in the Abrikosov graph in order to determine this).

8. The resulting expression can always be written as a sum (over internal particle indices) over terms of the form

$$\begin{aligned}
&\prod_{j=1}^{J} \frac{1}{\epsilon_{p_j} - \epsilon_p} \prod_{k=1}^{K} \frac{1}{-\epsilon_{q_k} + \epsilon_q} \prod_{l=1}^{L} \frac{1}{\epsilon_{p_l} - \epsilon_{q_l} - \epsilon_p + \epsilon_q} \prod_{m=1}^{M} \frac{1}{E_m + \epsilon_p} \\
\times\ & g(\omega) \\
\times\ & \prod_{j=1}^{J'} \frac{1}{-\epsilon_{t_j} + \epsilon_t} \prod_{k=1}^{K'} \frac{1}{\epsilon_{u_k} - \epsilon_u} \prod_{l=1}^{L'} \frac{1}{-\epsilon_{t_l} + \epsilon_{u_l} + \epsilon_t - \epsilon_u} \prod_{m=1}^{M'} \frac{1}{E'_m + \epsilon_s}
\end{aligned}$$

with a factor $g(\omega)$ which contains all the factors δ, n, $\bar{n}$, V and all denominators containing ω. The factors and after $g(\omega)$ have then to be replaced, taking into account that the denominators without E_m or E'_m could be zero, resulting in the final expression

$$\begin{aligned}
&\sum_{\substack{A\in\mathcal{P}(N_J)\\ B\in\mathcal{P}(N_K)\\ C\in\mathcal{P}(N_L)}} (-1)^{\#ABC} \prod_{\substack{j\in A\\ k\in B\\ l\in C}} \delta_{pp_j}\delta_{qq_k}\delta_{pq,p_lq_l} \prod_{\substack{j\in N_J\setminus A\\ k\in N_K\setminus B\\ l\in N_L\setminus C}} \bar{\delta}_{pp_j}\bar{\delta}_{qq_k}\bar{\delta}_{pq,p_lq_l} \\
&\quad \sum_{p\in P(\#ABC+1,M+N-\#ABC)} \prod_{k=1}^{M+N-\#ABC} \frac{1}{(\tilde{E}_k - \epsilon_p + \epsilon_q)^{p_k}} \\
\times\ & g(\omega) \\
\times\ & \sum_{\substack{A'\in\mathcal{P}(N_{J'})\\ B'\in\mathcal{P}(N_{K'})\\ C'\in\mathcal{P}(N_{L'})}} (-1)^{\#ABC'} \prod_{\substack{j\in A'\\ k\in B'\\ l\in C'}} \delta_{tt_j}\delta_{uu_k}\delta_{tu,t_lu_l} \prod_{\substack{j\in N_{J'}\setminus A'\\ k\in N_{K'}\setminus B'\\ l\in N_{L'}\setminus C'}} \bar{\delta}_{tt_j}\bar{\delta}_{uu_k}\bar{\delta}_{tu,t_lu_l} \\
&\quad \sum_{p\in P(\#ABC'+1,M'+N''-\#ABC')} \prod_{k=1}^{M'+N'-\#ABC'} \frac{1}{(\tilde{E}'_k + \epsilon_t - \epsilon_u)^{p_k}},
\end{aligned}$$

where

(a) $\#ABC = \#A + \#B + \#C$; $\#ABC' = \#A' + \#B' + \#C'$

(b) $N = J + K + L$; $N' = J' + K' + L'$

(c) $\tilde{E}_k = E_k$ for all $1 \le k \le M$; $\tilde{E}_{M+k} = \epsilon_{p_{j_k}}$ with $j_k \in N_J \setminus A$ for all $1 \le k \le J - \#A$, $j_1 \le j_2 \le \ldots \le j_{J-\#A}$; $\tilde{E}_{M+J-\#A+k} = \epsilon_{p_{j_k}}$ with $j_k \in N_K \setminus B$ for all $1 \le k \le$

$K - \#B$, $j_1 \leq_2 \leq \ldots \leq j_{K-\#B}$; $\tilde{E}_{M+J-\#A+K-\#B+k} = \epsilon_{p_{j_k}}$ with $j_k \in N_L \setminus C$ for all $1 \leq k \leq L - \#C$, $j_1 \leq_2 \leq \ldots \leq j_{L-\#C}$

(d) $\tilde{E}'_k = E'_k$ for all $1 \leq k \leq M'$; $\tilde{E}'_{M'+k} = \epsilon_{p_{j_k}}$ with $j_k \in N_{J'} \setminus A'$ for all $1 \leq k \leq J' - \#A'$, $j_1 \leq j_2 \leq \ldots \leq j_{J'-\#A'}$; $\tilde{E}'_{M'+J'-\#A'+k} = \epsilon_{p_{j_k}}$ with $j_k \in N_{K'} \setminus B'$ for all $1 \leq k \leq K' - \#B'$, $j_1 \leq_2 \leq \ldots \leq j_{K'-\#B'}$; $\tilde{E}'_{M'+J'-\#A'+K'-\#B'+k} = \epsilon_{p_{j_k}}$ with $j_k \in N_{L'} \setminus C'$ for all $1 \leq k \leq L' - \#C'$, $j_1 \leq_2 \leq \ldots \leq j_{L'-\#C'}$

The meaning of the rather obscure expressions in rule 8 is simple: the result of the evaluation gives a factor $g(\omega)$ for the part of the diagram between the time t and t' and two sums for the parts outside it. The first term in each sum is the result of the naive evaluation of the cuts. It has to be amended with factors $\bar{\delta}$ for every energy factor in the denominator which could become zero. For every other possible combination of factors δ and $\bar{\delta}$, additional summands appear, which are themselves sums over fractions. These fractions contain every possible combination of energy factors with the factors corresponding to the factor δ in the numerators left out, so that the total number of energy factor (counting every power separately) remains the same.

In the special case that $M = 0$, all energy factors appearing in the denominator can be zero. Hence no summand can appear in which all factors which could be zero are left out, because no factors would be left then in the denominator at all. The formula automatically gives this result, since the case where all factors are left out corresponds to $\#ABC = N$, and then we would have to sum over all partitions in $P(N+1, 0)$. But obviously, no such partitions exist.

The results of the above described evaluation provide the contributions in order n to

$$G_{rs}^{[q\bar{p},t\bar{u}]}(\omega) - \delta_{pu}\delta_{qt}G_{rs}^{[0,0]}(\omega - E^{[\bar{p}q]} + E^{[0]}).$$

On the other hand, by also including *some* of the disjoint diagrams (for details, see [18]), the results will be the contributions in order n to the quantity

$$G_{rs}^{[q\bar{p},t\bar{u}]}(\omega)$$

alone.

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