

# Functional derivative technique

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## I. THE SCHWINGER FUNCTIONAL DERIVATIVE TECHNIQUE

We will derive a closed set of equations which determine the self-energy by using the method of functional derivative, originally used by Schwinger in quantum electrodynamics and adopted into condensed matter by Hedin. The idea of the technique is to apply a time-dependent probing field to the system. The linear response of the one-particle Green's function with respect to the probing field can be related to the two-particle Green's function which in turn is related to the self-energy. Thus, the self-energy may be expressed as a functional derivative of the Green function with respect to the probing field. In the end, the field is set to zero since we only need to know the derivative calculated at zero field.

Since a time-dependent probing field is applied, it is convenient to work in the interaction representation. In the interaction representation the Green function is defined as

$$iG(1, 2) = \frac{\langle \Psi | T[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D(2)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle} \quad (1)$$

where

$$\hat{H} |\Psi\rangle = E_0 |\Psi\rangle, \quad (2)$$

$$\hat{S} = \hat{U}_D(\infty, -\infty), \quad (3)$$

$$\hat{U}_D(t, t') = T \exp[-i \int_{t'}^t d\tau \phi(\tau)] \quad (4)$$

$$\hat{\phi}(t) = \int d^3r \hat{\rho}(r, t) \varphi(r, t). \quad (5)$$

To simplify writing, we use the following notations:

$$r = (\mathbf{r}, \sigma), \quad (6)$$

$$1 = (r_1, t_1). \quad (7)$$

The field operators are in the interaction representation which is related to the field operators in the Heisenberg picture as follows (see Appendix):

$$\hat{\psi}_H(t) = \hat{U}_D(0, t)\hat{\psi}_D(t)\hat{U}_D(t, 0). \quad (8)$$

The ground state  $|\Psi\rangle$  is the *interacting* ground state without the probing field, i.e., it is the same as the Heisenberg ground state in the usual definition of the Green function:

$$iG(1, 2) = \frac{\langle \Psi | T[\hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)] | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (9)$$

It is important to note that the field operators in the Dirac picture are *independent* of the applied field  $\varphi(t)$  since

$$\hat{O}_D(t) = e^{i\hat{H}t}\hat{O}e^{-i\hat{H}t} \quad (10)$$

and that  $G$  depends on the applied field only through  $\hat{S}$ .

Let us relate the definition of  $G$  in (1) to the usual definition in (9). Using (8)

$$\begin{aligned} iG(1, 2) &= \frac{\langle \Psi | T[\hat{U}_D(\infty, 0)\hat{U}_D(0, t_1)\hat{\psi}_D(1)\hat{U}_D(t_1, 0)\hat{U}_D(0, t_2)\hat{\psi}_D^\dagger(2)\hat{U}_D(t_2, 0)\hat{U}_D(0, -\infty)] | \Psi \rangle}{\langle \Psi | \hat{U}_D(\infty, 0)\hat{U}_D(0, -\infty) | \Psi \rangle} \\ &= \frac{\langle \Psi_D(0) | T[\psi_H(1)\psi_H^\dagger(2)] | \Psi_D(0) \rangle}{\langle \Psi_D(0) | \Psi_D(0) \rangle} \\ &= \frac{\langle \Psi_H | T[\psi_H(1)\psi_H^\dagger(2)] | \Psi_H \rangle}{\langle \Psi_H | \Psi_H \rangle}. \end{aligned} \quad (11)$$

To obtain the third line we have utilised the condition that the state at  $t = \pm\infty$  is the interacting state without the probing field  $\varphi$  so that

$$|\Psi_D(0)\rangle = \hat{U}_D(0, -\infty)|\Psi\rangle, \quad \langle \Psi_D(0)| = \langle \Psi | \hat{U}_D(\infty, 0). \quad (12)$$

The above condition implies that  $\varphi(-t) = \varphi(t)$  up to a constant. The last line in (11) has been obtained from the fact that all pictures have their states coincide at  $t = 0$ . The above definition of the Green function is more general in that it includes the possibility of having a time-dependent probing field in the Hamiltonian. For  $\varphi \neq 0$ ,  $\Psi_D(0)$  is a state that has evolved, due to the probing field  $\varphi$ , from the interacting ground state at  $t = \pm\infty$  to a state at  $t = 0$ . There is no assumption about adiabatic continuity. The probing field  $\varphi$  is

arbitrary which may be large and rapidly varying in time. For  $\varphi = 0$  the above definition clearly reduces to (9) since  $\hat{S} \rightarrow 1$ ,  $\hat{\psi}_D \rightarrow \hat{\psi}_H$ , and  $\Psi_H$  becomes the interacting ground state  $\Psi$ . The Green function in (1) should be regarded as a functional of the probing field  $\varphi$ .

We will now take the functional derivative of  $G$  with respect to  $\varphi$ . In order to do this it is only necessary to work out the functional derivative of  $\hat{S}$  with respect to  $\varphi$  since the field operators in the Dirac picture do not depend on  $\varphi$ :

$$\begin{aligned} \frac{\delta \hat{S}}{\delta \varphi(3)} &= \frac{\delta}{\delta \varphi(3)} T \exp[-i \int d4 \hat{\rho}(4) \varphi(4)] \\ &= -iT[\hat{S}\hat{\rho}(3)]. \end{aligned} \quad (13)$$

We obtain

$$\begin{aligned} i \frac{\delta G(1, 2)}{\delta \varphi(3)} &= \frac{\delta}{\delta \varphi(3)} \frac{\langle \Psi | T[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D^\dagger(2)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle} \\ &= - \frac{i \langle \Psi | T[\hat{S}\hat{\rho}(3)\hat{\psi}_D(1)\hat{\psi}_D^\dagger(2)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle} \\ &\quad - \frac{i \langle \Psi | T[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D^\dagger(2)] | \Psi \rangle \langle \Psi | T[\hat{S}\hat{\rho}(3)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle^2} \end{aligned} \quad (14)$$

We define the two-particle Green's function as

$$G^{(2)}(1, 2, 3, 4) = (i)^2 \frac{\langle \Psi | T[\hat{S}\hat{\psi}_D(1)\hat{\psi}_D(3)\hat{\psi}_D^\dagger(4)\hat{\psi}_D^\dagger(2)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle}. \quad (15)$$

We therefore obtain

$$\frac{\delta G(1, 2)}{\delta \varphi(3)} = G(1, 2)\rho(3) - G^{(2)}(1, 2, 3, 3^+). \quad (16)$$

This relation is very important because it expresses the two-particle Green's function, which corresponds to the Coulomb term in the equation of motion of the Green function, as a linear response of the one-particle Green's function with respect to the probing field. It is readily verified that

$$G^{(2)}(1, 2, 3, 3^+) = \frac{\langle \Psi | T[\hat{S}\hat{\psi}_D(3)\hat{\psi}_D^\dagger(3^+)\hat{\psi}_D(1)\hat{\psi}_D^\dagger(2)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle}. \quad (17)$$

We now define the mass operator as follows:

$$i \int d3v(1-3)G^{(2)}(1, 2, 3, 3^+) = - \int d3M(1, 3)G(3, 2). \quad (18)$$

Multiplying both sides of the equation on the right by  $G^{-1}(2, 4)$  and integrating over the variable 2 we obtain

$$M(1, 4) = -i \int d3d2v(1-3)G^{(2)}(1, 2, 3, 3^+)G^{-1}(2, 4). \quad (19)$$

Using the relation in (16) we obtain

$$\begin{aligned} M(1, 4) &= -i \int d3d2v(1-3) \left[ G(1, 2)\rho(3) - \frac{\delta G(1, 2)}{\delta\varphi(3)} \right] G^{-1}(2, 4) \\ &= -i \int d3v(1-3)\rho(3)\delta(1-4) + i \int d3d2v(1-3) \frac{\delta G(1, 2)}{\delta\varphi(3)} G^{-1}(2, 4) \\ &= V_H(1)\delta(1-4) + i \int d3d2v(1-3) \frac{\delta G(1, 2)}{\delta\varphi(3)} G^{-1}(2, 4). \end{aligned} \quad (20)$$

Thus, by replacing the two-particle Green's function using (16) the mass operator is now expressed entirely in terms of the single-particle Green's function and its functional derivative with respect to the probing field. The self-energy is defined as the mass operator less the Hartree potential:

$$\Sigma(1, 2) = i \int d3d4v(1-3) \frac{\delta G(1, 4)}{\delta\varphi(3)} G^{-1}(4, 2). \quad (21)$$

Since

$$\int d4G(1, 4)G^{-1}(4, 2) = \delta(1-2) \quad (22)$$

it follows that

$$\int d4 \left[ \frac{\delta G(1, 4)}{\delta\varphi(3)} G^{-1}(4, 2) + G(1, 4) \frac{\delta G^{-1}(4, 2)}{\delta\varphi(3)} \right] = 0. \quad (23)$$

$$\frac{\delta G(1, 2)}{\delta\varphi(3)} = - \int d4d5 G(1, 4) \frac{\delta G^{-1}(4, 5)}{\delta\varphi(3)} G(5, 2) \quad (24)$$

We may write

$$\Sigma(1, 2) = -i \int d3d4v(1-3)G(1, 4) \frac{\delta G^{-1}(4, 2)}{\delta\varphi(3)}. \quad (25)$$

From the equation of motion we have (Exercise 1)

$$\left( i \frac{\partial}{\partial t_1} - h(1) \right) G(1, 2) - \int d3 \Sigma(1, 3)G(3, 2) = \delta(1-2), \quad (26)$$

where  $h$  is the one-particle part of the Hamiltonian that includes the probing field  $\varphi$ :

$$h = -\frac{1}{2}\nabla^2 + V_{ext} + V_H + \varphi.$$

Multiplying both sides on the right by the inverse of  $G$  yields

$$G^{-1}(1, 2) = \left( i \frac{\partial}{\partial t_1} - h(1) \right) \delta(1-2) - \Sigma(1, 2) \quad (27)$$

and therefore, using  $\delta\varphi(1)/\delta\varphi(3) = \delta(1-3)$ ,

$$\frac{\delta G^{-1}(1,2)}{\delta\varphi(3)} = - \left[ \delta(1-3) + \frac{\delta V_H(1)}{\delta\varphi(3)} \right] \delta(1-2) - \frac{\delta\Sigma(1,2)}{\delta\varphi(3)}. \quad (28)$$

Using this expression in (25) gives

$$\begin{aligned} \Sigma(1,2) &= i \int d3d4v(1-3)G(1,4) \left[ \left\{ \delta(4-3) + \frac{\delta V_H(4)}{\delta\varphi(3)} \right\} \delta(4-2) + \frac{\delta\Sigma(4,2)}{\delta\varphi(3)} \right] \\ &= iv(1-2)G(1,2) + i \int d3v(1-3)G(1,2) \frac{\delta V_H(2)}{\delta\varphi(3)} \\ &\quad + i \int d3d4v(1-3)G(1,4) \frac{\delta\Sigma(4,2)}{\delta\varphi(3)}. \end{aligned} \quad (29)$$

This is an *iterative* equation for the self-energy which provides a procedure for making an expansion of the self-energy in powers of the Coulomb interaction. We recognised that the first term is just the exchange potential. It is a more general form of exchange with an interacting Green's function instead of a non-interacting one.

Let us work out the self-energy to second order in  $v$  and show that it is consistent with the conventional perturbation expansion result. In order to do this, we need to calculate  $\delta V_H/\delta\phi$  and  $\delta\Sigma/\delta\phi$  to first order in  $v$ , as can be seen from (29).

$$\begin{aligned} \frac{\delta V_H(2)}{\delta\varphi(3)} &= \int d4 v(2-4) \frac{\delta\rho(4)}{\delta\varphi(3)} \\ &= -i \int d4 v(2-4) \frac{\delta G(4,4^+)}{\delta\varphi(3)} \\ &= i \int d4d5d6 v(2-4)G(4,5) \frac{\delta G^{-1}(5,6)}{\delta\varphi(3)} G(6,4^+). \end{aligned} \quad (30)$$

where the identity in (23) has been used in the last line. To first order in  $v$ ,

$$\frac{\delta V_H(2)}{\delta\varphi(3)} = -i \int d4 v(2-4)G(4,3)G(3,4^+). \quad (31)$$

To first order  $\Sigma = ivG$  and using this we calculate

$$\frac{\delta\Sigma(4,2)}{\delta\varphi(3)} = iv(4-2) \frac{\delta G(4,2)}{\delta\varphi(3)}. \quad (32)$$

Using (24)

$$\begin{aligned} \frac{\delta\Sigma(4,2)}{\delta\varphi(3)} &= -i \int d5d6 v(4-2)G(4,5) \frac{\delta G^{-1}(5,6)}{\delta\varphi(3)} G(6,2) \\ &= i \int d5d6 v(4-2)G(4,5) \\ &\quad \times \left[ \delta(5-6) \left\{ \delta(5-3) + \frac{\delta V_H(5)}{\delta\varphi(3)} \right\} + \frac{\delta\Sigma(5,6)}{\delta\varphi(3)} \right] G(6,2) \\ &= iv(4-2)G(4,3)G(3,2) + O(v^2). \end{aligned}$$

Using the result for  $\delta V_H/\delta\phi$  and  $\delta\Sigma/\delta\phi$  in (29) and keeping terms up to second order in  $v$  we obtain

$$\begin{aligned}
\Sigma(1,2) &= iv(1-2)G(1,2) + i \int d3v(1-3)G(1,2) \frac{\delta V_H(2)}{\delta\varphi(3)} \\
&+ i \int d3d4v(1-3)G(1,4) \frac{\delta\Sigma(4,2)}{\delta\varphi(3)} \\
&= iv(1-2)G(1,2) \\
&+ i \int d3v(1-3)G(1,2)(-i) \int d4 v(2-4)G(4,3)G(3,4^+) \\
&+ i \int d3d4v(1-3)G(1,4)iv(4-2)G(4,3)G(3,2). \tag{33}
\end{aligned}$$

This is consistent with the result obtained using the traditional diagrammatic expansion. Since  $G$  is the interacting Green's function, the self-energy consists only of *skeleton* diagrams. A skeleton diagram cannot be reduced further by absorbing interactions into renormalised Green function lines.

The Schwinger functional derivative technique has several advantages over the conventional diagrammatic technique. The iterative equation for the self-energy in (29) is exact and it allows us to generate all the terms in the perturbation expansion without the need to enumerate topologically distinct connected diagrams and to employ the tedious Wick's theorem. Moreover, the ground state in the definition of the Green function in the interaction picture in (1) is the exact *interacting* ground state. There is no assumption of adiabatic continuity, associated with switching on the Coulomb interaction slowly from  $t = \pm\infty$  to  $t = 0$ , that is needed to make a one-to-one connection between the non-interacting ground state and the interacting one. The probing field  $\varphi$  in the functional derivative technique can be large and rapidly varying in time. Its role is to probe the response of the system, not to connect a non-interacting ground state to an interacting one. The Schwinger functional derivative technique provides a simple and elegant way of deriving the self-energy.

## II. THE HEDIN EQUATIONS

The self-energy expression presented in the previous section was derived by Hedin. It was already realised at that time that a finite expansion in powers of the bare Coulomb interaction  $v$  leads to unphysical results in solids. The reason is that in solids screening effects are of paramount importance. At low energies, the effective Coulomb interaction is

much smaller than the bare value, especially for metals. It was then proposed by Hedin that one should make an expansion of the self-energy in powers of the *screened* interaction. Since the screened interaction is much weaker than the bare one the self-energy may be expected to converge much faster. This turns out to be not the case, due to the presence of energy dependence in the screened interaction. Nevertheless the Hedin equations, which are a set of self-consistent equations relating the self-energy to the screened interaction, provide a powerful tool for studying the electronic structure of matter from first-principles.

Instead of  $\varphi$  it is permissible to work with the total field

$$V = \varphi + V_H. \quad (34)$$

In place of (28) we have

$$\frac{\delta G^{-1}(1, 2)}{\delta V(3)} = -\delta(1 - 2)\delta(1 - 3) - \frac{\delta \Sigma(1, 2)}{\delta V(3)}. \quad (35)$$

Using the chain rule the self-energy in (25) becomes

$$\Sigma(1, 2) = -i \int d3d4d5 v(1 - 3)G(1, 4) \frac{\delta G^{-1}(4, 2)}{\delta V(5)} \frac{\delta V(5)}{\delta \varphi(3)}. \quad (36)$$

$\delta V/\delta \varphi$  is simply the definition of the inverse dielectric function: it is the ratio between the total and the applied fields.

$$\epsilon^{-1}(1, 2) \equiv \frac{\delta V(1)}{\delta \varphi(2)}. \quad (37)$$

The Coulomb interaction is then screened by the dielectric function.

$$\int d3 v(1 - 3) \frac{\delta V(5)}{\delta \varphi(3)} = \int d3 \epsilon^{-1}(5, 3)v(3 - 1) \equiv W(5, 1).$$

Thus,

$$\Sigma(1, 2) = i \int d4d5 W(5, 1)G(1, 4)\Lambda(4, 2, 5), \quad (38)$$

where we have defined the vertex function  $\Lambda$  as

$$\begin{aligned} \Lambda(1, 2, 3) &\equiv -\frac{\delta G^{-1}(1, 2)}{\delta V(3)} \\ &= \delta(1 - 2)\delta(1 - 3) + \frac{\delta \Sigma(1, 2)}{\delta V(3)}. \end{aligned} \quad (39)$$



Using the chain rule and the identity in (23) we can set up an integral equation for the vertex.

$$\begin{aligned}
\Lambda(1, 2, 3) &= \delta(1-2)\delta(1-3) + \frac{\delta\Sigma(1, 2)}{\delta V(3)} \\
&= \delta(1-2)\delta(1-3) + \int d4d5 \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} \frac{\delta G(4, 5)}{\delta V(3)} \\
&= \delta(1-2)\delta(1-3) - \int d4d5 \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} \int d6d7 G(4, 6) \frac{\delta G^{-1}(6, 7)}{\delta V(3)} G(7, 5) \\
&= \delta(1-2)\delta(1-3) + \int d4d5d6d7 \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Lambda(6, 7, 3). \tag{40}
\end{aligned}$$

We now need an integral equation that determines the screened interaction  $W$ . From (37)

$$W(1, 2) = \int d3 \epsilon^{-1}(1, 3) v(3-2) = \int d3 \frac{\delta V(1)}{\delta \varphi(3)} v(3-2) \tag{41}$$

and using (34)

$$\begin{aligned}
W(1, 2) &= \int d3 \left[ \delta(1-3) + \frac{\delta V_H(1)}{\delta \varphi(3)} \right] v(3-2) \\
&= v(1-2) + \int d3d4 v(1-4) \frac{\delta \rho(4)}{\delta \varphi(3)} v(3-2) \\
&= v(1-2) + \int d3d4d5 v(1-4) \frac{\delta \rho(4)}{\delta V(5)} \frac{\delta V(5)}{\delta \varphi(3)} v(3-2) \\
&= v(1-2) + \int d3d4 d5 v(1-4) \frac{\delta \rho(4)}{\delta V(5)} \epsilon^{-1}(5, 3) v(3-2) \\
&= v(1-2) + \int d4d5 v(1-4) P(4, 5) W(5, 2) \tag{42}
\end{aligned}$$

where we have defined the polarisation function

$$P(1, 2) \equiv \frac{\delta \rho(1)}{\delta V(2)}. \tag{43}$$

The linear density response function, hereafter referred to as response function, is defined as

$$R(1, 2) \equiv \frac{\delta \rho(1)}{\delta \varphi(2)}. \tag{44}$$

The polarisation function is the response function with respect to the *total* field. We can

readily write down the integral equation for the response function from its definition.

$$\begin{aligned}
R(1, 2) &= \frac{\delta\rho(1)}{\delta\varphi(2)} \\
&= \int d3 \frac{\delta\rho(1)}{\delta V(3)} \frac{\delta V(3)}{\delta\varphi(2)} \\
&= \int d3 P(1, 3) \left[ \delta(3-2) + \int d4 v(3-4) \frac{\delta\rho(4)}{\delta\varphi(2)} \right] \\
&= P(1, 2) + \int d3 d4 P(1, 3) v(3-4) R(4, 2),
\end{aligned} \tag{45}$$

which is identical in form to the integral equation for the screened interaction.

The polarisation function can be expressed in terms of the Green function.

$$\begin{aligned}
P(1, 2) &= \frac{\delta\rho(1)}{\delta V(2)} \\
&= -i \frac{\delta G(1, 1^+)}{\delta V(2)} \\
&= i \int d3 d4 G(1, 3) \frac{\delta G^{-1}(3, 4)}{\delta V(2)} G(4, 1^+) \\
&= -i \int d3 d4 G(1, 3) \Lambda(3, 4, 2) G(4, 1^+).
\end{aligned} \tag{46}$$

From the definition of the screened interaction

$$\begin{aligned}
W(1, 2) &= \int d3 \epsilon^{-1}(1, 3) v(3-2) \\
&= \int d3 \frac{\delta V(1)}{\delta\varphi(3)} v(3-2) \\
&= \int d3 \left[ \delta(1-3) + \frac{\delta V_H(1)}{\delta\varphi(3)} \right] v(3-2) \\
&= v(1-2) + \int d3 d4 v(1-4) R(4, 3) v(3-2)
\end{aligned} \tag{47}$$

In summary, the closed set of self-consistent Hedin's equations is given by

$$\Sigma(1, 2) = i \int d4 d5 W(5, 1) G(1, 4) \Lambda(4, 2, 5). \tag{48}$$

$$\Lambda(1, 2, 3) = \delta(1-2) \delta(1-3) \tag{49}$$

$$+ \int d4 d5 d6 d7 \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Lambda(6, 7, 3). \tag{50}$$

$$W(1, 2) = v(1 - 2) + \int d3d4 v(1 - 3)P(3, 4)W(4, 2). \quad (51)$$

$$P(1, 2) = -i \int d3d4 G(1, 3)\Lambda(3, 4, 2)G(4, 1^+). \quad (52)$$

$$G(1, 2) = G^0(1, 2) + \int d3d4 G^0(1, 3)\Sigma(3, 4)G(4, 2). \quad (53)$$

The non-interacting Green function  $G^0$  is defined to be the Hartree Green function.

### III. PHYSICAL SIGNIFICANCE OF $W$

The screened interaction is given by

$$W(1, 2) = v(1 - 2) + \int d3d4 v(1 - 3)R(3, 4)v(4 - 2) \quad (54)$$

We can think of  $v(1 - 2)$  as the Coulomb potential at 1 of a test charge located at 2, which may be chosen to be at the origin of the coordinate system:

$$W(1) = v(1) + \int d3d4 v(1 - 3)R(3, 4)v(4)$$

Consider

$$\delta\rho(3) = \int d4R(3, 4)v(4)$$

in the second term on the right hand side. This is the induced charge density of the system at point 3 due to the presence of the test charge at 2, which has been chosen to be at the origin. This induced charge density gives rise to a change in the Hartree potential at point 1:

$$\delta V_H(1) = \int d3v(1 - 3)\delta\rho(3),$$

which acts as a screening potential for the test charge so that the total potential of the test charge is given by the screened interaction

$$W(1) = v(1) + \delta V_H(1).$$

Thus,  $W(1, 2)$  is a screened potential at point 1 of a test charge located at point 2.

#### IV. LINEAR RESPONSE THEORY: THE KUBO FORMULA

We will derive the Kubo formula in two ways, following the original derivation of Kubo and using the Schwinger functional derivative method. As will be seen, the latter technique provides a much simpler way of deriving the formula.

Consider applying an external field  $\varphi(\mathbf{r}, t)$ , which may be time dependent, to a system in its ground state. We wish to work out a formula which allows us to calculate the change in a physical quantity represented by an operator  $\hat{O}$  to first order in the applied field. Since we apply an external field, it is convenient to work in the interaction picture. The equation of motion of the state vector in the interaction representation is given by

$$i \frac{\partial}{\partial t} |\Psi_D(t)\rangle = \hat{\phi}_D(t) |\Psi_D(t)\rangle \quad (55)$$

where

$$\hat{\phi}_D(t) = e^{i\hat{H}t} \hat{\phi}(t) e^{-i\hat{H}t}. \quad (56)$$

The formal solution to the time-development of the state vector is given by

$$|\Psi_D(t)\rangle = \hat{U}_D(t, 0) |\Psi_D(0)\rangle \quad (57)$$

where

$$\hat{U}(t, 0) = T e^{-i \int_0^t dt' \hat{\phi}_D(t')}. \quad (58)$$

The expectation value of an operator  $\hat{O}$  at time  $t$  is then

$$\begin{aligned} O(t) &= \langle \Psi_D(t) | \hat{O}_D(t) | \Psi_D(t) \rangle \\ &= \langle \Psi_D(0) | \hat{U}(0, t) \hat{O}_D(t) \hat{U}(t, 0) | \Psi_D(0) \rangle \end{aligned} \quad (59)$$

where

$$\hat{O}_D(t) = e^{i\hat{H}t} \hat{O} e^{-i\hat{H}t}. \quad (60)$$

To first order in the applied field the time-development operator is given by

$$\hat{U}_D(t, 0) = 1 - i \int_0^t dt' \hat{\phi}_D(t'), \quad (61)$$

$$\hat{U}_D(0, t) = \hat{U}_D^\dagger(t, 0) = 1 + i \int_0^t dt' \hat{\phi}_D(t'). \quad (62)$$

Substituting these in the expression for  $O(t)$  yields

$$\begin{aligned}\delta O(t) &= \left\langle \Psi_D(t) | \hat{O}_D(t) | \Psi_D(t) \right\rangle - \left\langle \Psi_D(0) | \hat{O}_D(t) | \Psi_D(0) \right\rangle \\ &= i \int_0^t dt' \left\langle \Psi_D(0) | [\hat{\phi}_D(t'), \hat{O}_D(t)] | \Psi_D(0) \right\rangle.\end{aligned}\quad (63)$$

Note that

$$\begin{aligned}\left\langle \Psi_D(0) | \hat{O}_D(t) | \Psi_D(0) \right\rangle &= \left\langle \Psi | e^{i\hat{H}t} \hat{O} e^{-i\hat{H}t} | \Psi \right\rangle \\ &= \left\langle \Psi | e^{iE_0 t} \hat{O} e^{-iE_0 t} | \Psi \right\rangle \\ &= \left\langle \Psi | \hat{O} | \Psi \right\rangle.\end{aligned}$$

We recall that the Dirac operators are the same as the Heisenberg operators *without* the applied field and all representations have the same state at  $t = 0$  so that  $\Psi_D(0)$  is just the interacting ground state without the applied field.

Let us consider an external field that is coupled to the charge density, i.e.,

$$\hat{\phi}_D(t) = \int dr \hat{\psi}_D^\dagger(rt) \varphi(rt) \hat{\psi}_D(rt) = \int dr \varphi(rt) \hat{\rho}_D(rt), \quad (64)$$

and let us calculate the density response to this applied field. Using  $\hat{O}_D = \hat{\rho}_D$  in (63) we find

$$\begin{aligned}\delta\rho(rt) &= i \int_0^t dt' \left\langle \Psi_D(0) | [\hat{\phi}_D(t'), \hat{\rho}_D(rt)] | \Psi_D(0) \right\rangle \\ &= i \int dr' \int_0^t dt' \varphi(r't') \left\langle \Psi_D(0) | [\hat{\rho}_D(r't'), \hat{\rho}_D(rt)] | \Psi_D(0) \right\rangle.\end{aligned}\quad (65)$$

The retarded linear density response function  $R^r(rt, r't')$  is defined by

$$\delta\rho(rt) = \int dr' \int_0^\infty dt' R^r(rt, r't') \varphi(r't') \quad (66)$$

so that

$$\begin{aligned}R^r(rt, r't') &= i \left\langle \Psi_D(0) | [\hat{\rho}_D(r't'), \hat{\rho}_D(rt)] | \Psi_D(0) \right\rangle \theta(t - t') \\ &= i \left\langle \Psi | [\hat{\rho}_H(r't'), \hat{\rho}_H(rt)] | \Psi \right\rangle \theta(t - t')\end{aligned}\quad (67)$$

is the *retarded* response function. The second line is obtained by setting the probing field  $\varphi$  to zero.

As another demonstration of the usefulness of the Schwinger functional derivative technique, we can readily derive the Kubo formula from (14). Since  $\rho(1) = -iG(1, 1^+)$  the linear density response  $R = \delta\rho/\delta\phi$  is

$$\begin{aligned}
R(1, 2) &= -i \frac{\delta G(1, 1^+)}{\delta\phi(2)} \\
&= \frac{\delta}{\delta\phi(2)} \frac{\langle \Psi | T[\hat{S}\hat{\rho}_D(1)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle} \\
&= - \frac{i \langle \Psi | T[\hat{S}\hat{\rho}_D(2)\hat{\rho}_D(1)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle} \\
&\quad + \frac{i \langle \Psi | T[\hat{S}\hat{\rho}_D(1)] | \Psi \rangle \langle \Psi | T[\hat{S}\hat{\rho}_D(2)] | \Psi \rangle}{\langle \Psi | \hat{S} | \Psi \rangle^2}
\end{aligned} \tag{68}$$

After taking the functional derivative of the density  $\rho_D(1) = -iG(1, 1^+)$  with respect to the applied field  $\varphi$ , we set  $\varphi = 0$ . This implies that  $\hat{S} = 1$  and the Dirac field operator becomes the Heisenberg field operator. We obtain without much effort the time-ordered linear density response function

$$R(1, 2) = -i \langle \Psi | \Delta\hat{\rho}_H(2)\Delta\hat{\rho}_H(1) | \Psi \rangle \theta(t_2 - t_1) - i \langle \Psi | \Delta\hat{\rho}_H(1)\Delta\hat{\rho}_H(2) | \Psi \rangle \theta(t_1 - t_2) \tag{69}$$

where

$$\Delta\hat{\rho}_H = \hat{\rho}_H - \rho \tag{70}$$

is the density fluctuation operator measuring the density fluctuation from the ground-state density  $\rho(1) = \langle \Psi | \hat{\rho}_H(1) | \Psi \rangle$ .

To obtain the response function in the frequency representation we first insert a complete

set of eigenstates of  $\hat{H}$  in between the density operators yielding

$$\begin{aligned}
& \langle \Psi | \Delta \hat{\rho}_H(2) \Delta \hat{\rho}_H(1) | \Psi \rangle \theta(t_2 - t_1) + \langle \Psi | \Delta \hat{\rho}_H(1) \Delta \hat{\rho}_H(2) | \Psi \rangle \theta(t_1 - t_2) \\
&= \sum_n \langle \Psi | \Delta \hat{\rho}_H(2) | n \rangle \langle n | \Delta \hat{\rho}_H(1) | \Psi \rangle \theta(t_2 - t_1) \\
&+ \sum_n \langle \Psi | \Delta \hat{\rho}_H(1) | n \rangle \langle n | \Delta \hat{\rho}_H(2) | \Psi \rangle \theta(t_1 - t_2) \\
&= \sum_n \left\langle \Psi | e^{i\hat{H}t_2} \Delta \hat{\rho}(r_2) e^{-i\hat{H}t_2} | n \rangle \langle n | e^{i\hat{H}t_1} \Delta \hat{\rho}(r_1) e^{-i\hat{H}t_1} | \Psi \right\rangle \theta(t_2 - t_1) \\
&+ \sum_n \left\langle \Psi | e^{i\hat{H}t_1} \Delta \hat{\rho}(r_1) e^{-i\hat{H}t_1} | n \rangle \langle n | e^{i\hat{H}t_2} \Delta \hat{\rho}(r_2) e^{-i\hat{H}t_2} | \Psi \right\rangle \theta(t_1 - t_2) \\
&= \sum_n \langle \Psi | \Delta \hat{\rho}(r_2) | n \rangle \langle n | \Delta \hat{\rho}(r_1) | \Psi \rangle e^{-i(E_n - E_0)(t_2 - t_1)} \theta(t_2 - t_1) \\
&+ \sum_n \langle \Psi | \Delta \hat{\rho}(r_1) | n \rangle \langle n | \Delta \hat{\rho}(r_2) | \Psi \rangle e^{-i(E_n - E_0)(t_1 - t_2)} \theta(t_1 - t_2)
\end{aligned} \tag{71}$$

Performing the Fourier transform as in the Lehman representation of the Green function yields the famous Kubo's formula

$$R(r, r'; \omega) = \sum_n \left[ \frac{\langle \Psi | \Delta \hat{\rho}(r') | n \rangle \langle n | \Delta \hat{\rho}(r) | \Psi \rangle}{\omega - E_n + E_0 + i\eta} - \frac{\langle \Psi | \Delta \hat{\rho}(r) | n \rangle \langle n | \Delta \hat{\rho}(r') | \Psi \rangle}{\omega + E_n - E_0 - i\eta} \right] \tag{72}$$

The response function gives information about the excitation spectrum of the system.  $\text{Im} R(\omega)$  exhibits peaks when  $\omega = E_n - E_0$ , corresponding to the  $N$ -particle excitation energies.

If there is no magnetic field, i.e., if time-reversal symmetry is obeyed,

$$\langle \Psi | \Delta \hat{\rho}(r') | n \rangle \langle n | \Delta \hat{\rho}(r) | \Psi \rangle = \langle \Psi | \Delta \hat{\rho}(r) | n \rangle \langle n | \Delta \hat{\rho}(r') | \Psi \rangle \tag{73}$$

is real so that  $R$  satisfies

$$R(r, r'; -\omega) = R(r, r'; \omega), \tag{74}$$

$$R(r, r'; \omega) = R(r', r; \omega). \tag{75}$$

The response function  $R$  is the *time-ordered* response which differs from the *retarded* response  $R^r$ . The two are related as follows:

$$\text{Re} R(\omega) = \text{Re} R^r(\omega), \tag{76}$$

$$\text{Im} R(\omega) \text{sgn}(\omega) = \text{Im} R^r(\omega), \quad \text{sgn}(\omega) \equiv \omega/|\omega| \tag{77}$$

valid for real  $\omega$ .

Compared with the original derivation of Kubo, the Schwinger functional derivative technique provides a simple way of deriving the response functions. We have derived the Kubo formula specifically for linear density response function. However, the method is applicable to a more general response function since any expectation value of a single-particle operator in the ground state is expressible in terms of the Green function.

The response function can be written in terms of its spectral representation.

$$R(r, r'; \omega) = \int_{-\infty}^0 d\omega' \frac{S(r, r'; \omega')}{\omega - \omega' - i\eta} + \int_0^{\infty} d\omega' \frac{S(r, r'; \omega')}{\omega - \omega' + i\eta} \quad (78)$$

$$S(r, r'; \omega' \geq 0) = \sum_n \langle \Psi | \Delta \hat{\rho}(r') | n \rangle \langle n | \Delta \hat{\rho}(r) | \Psi \rangle \delta(\omega' - E_n + E_0) \quad (79)$$

To ensure the symmetry of  $R$  we *define*

$$S(r, r'; -\omega) = -S(r, r'; \omega). \quad (80)$$

It can be readily verified that the spectral representation of  $R$  is equivalent to (72). The spectral function  $S(r, r'; \omega)$  is *real* for systems with time reversal symmetry. Using the symmetry property of the spectral function the spectral representation of  $R$  can be rewritten as

$$R(r, r'; \omega) = \int_0^{\infty} d\omega' S(r, r'; \omega') \left\{ \frac{1}{\omega - \omega' + i\eta} - \frac{1}{\omega + \omega' - i\eta} \right\}. \quad (81)$$

### A. The Random-Phase Approximation (Time-Dependent Hartree Approximation)

When we perturb a system of electrons by applying an external field, the density will change and the change in the density can be calculated if we know the response function of the system. In many cases it is sufficient to calculate the linear response function as defined in (66). However, as the perturbation field becomes larger, non-linear response functions may become important. The random-phase approximation (RPA) is an approximation for the linear response function. It was originally derived for the electron gas by Bohm and Pines using the equation of motion method. Gell-Mann and Brueckner subsequently derived the RPA using the many-body diagrammatic technique. The derivation is very involved and



requires the assumption that the electron density is high, much higher than the average electron density found in the alkali metals and in most materials. In fact, the RPA is equivalent to the time-dependent Hartree approximation (TDHA), which does not require the assumption of high electron density. Here, we derive the RPA using the functional derivative method, yet another demonstration of the usefulness of the method.

The linear response function is given by

$$R(1, 2) = \frac{\delta\rho(1)}{\delta\varphi(2)}. \quad (82)$$

In terms of the Green function the density is given by

$$\rho(1) = -iG(1, 1^+). \quad (83)$$

Thus taking the functional derivative we obtain

$$\begin{aligned} R(1, 2) &= -i \frac{\delta G(1, 1^+)}{\delta\varphi(2)} \\ &= i \int d3d4 G(1, 3) \frac{\delta G^{-1}(3, 4)}{\delta\varphi(2)} G(4, 1^+) \\ &= -i \int d3d4 G(1, 3) \left[ \delta(3-4)\delta(3-2) + \delta(3-4) \frac{\delta V_H(4)}{\delta\varphi(2)} + \frac{\delta\Sigma(3, 4)}{\delta\varphi(2)} \right] G(4, 1^+). \end{aligned} \quad (84)$$

The second step has been obtained using the identity in (23) and the third step from (28). The RPA corresponds to neglecting the response of the self-energy  $\Sigma$  to the applied field  $\varphi$ , keeping only the change in the Hartree potential with respect to the applied field. This is why we may regard the RPA as the time-dependent Hartree approximation. In this approximation we have

$$\begin{aligned} R(1, 2) &= -i \int d3 G(1, 3)G(3, 1^+) \left[ \delta(3-2) + \frac{\delta V_H(3)}{\delta\varphi(2)} \right] \\ &= \int d3 P(1, 3) \left[ \delta(3-2) + \frac{\delta V_H(3)}{\delta\varphi(2)} \right] \\ &= P(1, 2) + \int d3d4 P(1, 3)v(3-4) \frac{\delta\rho(4)}{\delta\varphi(2)}. \end{aligned} \quad (85)$$

Thus we obtain the well-known RPA equation

$$R(1, 2) = P(1, 2) + \int d3d4 P(1, 3)v(3-4)R(4, 2), \quad (86)$$

with

$$P(1, 2) = -iG(1, 2)G(2, 1^+), \quad (87)$$

which is equivalent to approximating the vertex in (46) by

$$\Lambda(1, 2, 3) = \delta(1 - 2)\delta(1 - 3). \quad (88)$$

We note that the *form* of the RPA equation is the same as the exact equation for the response function in (45). The difference lies in  $P$ , where the vertex function  $\Lambda$  is approximated by (88).

If we solve (86) iteratively, we obtain

$$R = P + PvP + PvPvP + \dots \quad (89)$$

If we represent the right hand side by diagrams, we obtain the so-called ring diagrams, where each ring diagram represents the polarisation  $P = -iGG$  and the two lines forming the ring represent the Green functions  $G$ .

Let us work out the polarisation function explicitly using some non-interacting  $G^0$ . In practice this is chosen to be the LDA Green function. The Fourier expansion of the Green function is

$$G(1, 2) = \int \frac{d\omega}{2\pi} e^{-i\omega(t_1-t_2)} G(r_1, r_2; \omega). \quad (90)$$

$$P(1, 2) = -i \int \frac{d\omega_1}{2\pi} e^{-i\omega_1(t_1-t_2)} G(r_1, r_2; \omega_1) \int \frac{d\omega_2}{2\pi} e^{-i\omega_2(t_2-t_1)} G(r_2, r_1; \omega_2). \quad (91)$$

Taking the Fourier transform of  $P$  yields, with  $\tau = t_1 - t_2$

$$\begin{aligned} P(r_1, r_2; \omega) &= \int d\tau e^{i\omega\tau} P(r_1, r_2; \tau) \\ &= -i \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} d\tau e^{i(\omega-\omega_1+\omega_2)\tau} G(r_1, r_2; \omega_1) G(r_2, r_1; \omega_2) \\ &= -i \int \frac{d\omega_1}{2\pi} \frac{d\omega_2}{2\pi} 2\pi\delta(\omega - \omega_1 + \omega_2) G(r_1, r_2; \omega_1) G(r_2, r_1; \omega_2) \\ &= -i \int \frac{d\omega_2}{2\pi} G(r_1, r_2; \omega + \omega_2) G(r_2, r_1; \omega_2). \end{aligned} \quad (92)$$

which also follows directly from the convolution theorem. Using a non-interacting Green's function

$$G^0(r, r'; \omega) = \sum_{\mathbf{kn}}^{\text{occ}} \frac{\phi_{\mathbf{kn}}(r)\phi_{\mathbf{kn}}^*(r')}{\omega - \varepsilon_{\mathbf{kn}} - i\delta} + \sum_{\mathbf{kn}}^{\text{unocc}} \frac{\phi_{\mathbf{kn}}(r)\phi_{\mathbf{kn}}^*(r')}{\omega - \varepsilon_{\mathbf{kn}} + i\delta}. \quad (93)$$

the integral over the frequency  $\omega_2$  consists of four terms of the form

$$\int d\omega_2 \left( \frac{1}{\omega + \omega_2 - \varepsilon_{\mathbf{k}n} - i\delta} \right)_{\text{occ}} \times \left( \frac{1}{\omega_2 - \varepsilon_{\mathbf{k}'n'} - i\delta} \right)_{\text{occ}}, \quad (94)$$

$$\int d\omega_2 \left( \frac{1}{\omega + \omega_2 - \varepsilon_{\mathbf{k}n} - i\delta} \right)_{\text{occ}} \times \left( \frac{1}{\omega_2 - \varepsilon_{\mathbf{k}'n'} + i\delta} \right)_{\text{unocc}}, \quad (95)$$

$$\int d\omega_2 \left( \frac{1}{\omega + \omega_2 - \varepsilon_{\mathbf{k}n} + i\delta} \right)_{\text{unocc}} \times \left( \frac{1}{\omega_2 - \varepsilon_{\mathbf{k}'n'} - i\delta} \right)_{\text{occ}}, \quad (96)$$

$$\int d\omega_2 \left( \frac{1}{\omega + \omega_2 - \varepsilon_{\mathbf{k}n} + i\delta} \right)_{\text{unocc}} \times \left( \frac{1}{\omega_2 - \varepsilon_{\mathbf{k}'n'} + i\delta} \right)_{\text{unocc}}. \quad (97)$$

The integrand of the first integral has both of its poles in the upper-half plane so that the integral is zero because the contour can be chosen to be along a semicircle in the lower-half plane. The integrand of the fourth integral has both of its poles in the lower-half plane and by choosing the contour to be along a semicircle in the upper-half plane the integral is also zero. Only the second and third integrals are non-zero. Performing the second contour integral by closing the contour in the lower-half semicircle yields

$$\begin{aligned} & \int d\omega_2 \left( \frac{1}{\omega + \omega_2 - \varepsilon_{\mathbf{k}n} - i\delta} \right)_{\text{occ}} \times \left( \frac{1}{\omega_2 - \varepsilon_{\mathbf{k}'n'} + i\delta} \right)_{\text{unocc}} \\ &= -\frac{2\pi i}{\omega + \varepsilon_{\mathbf{k}'n'}^{\text{unocc}} - \varepsilon_{\mathbf{k}n}^{\text{occ}} - i\delta}. \end{aligned} \quad (98)$$

Similarly

$$\begin{aligned} & \int d\omega_2 \left( \frac{1}{\omega + \omega_2 - \varepsilon_{\mathbf{k}n} + i\delta} \right)_{\text{unocc}} \times \left( \frac{1}{\omega_2 - \varepsilon_{\mathbf{k}'n'} - i\delta} \right)_{\text{occ}} \\ &= \frac{2\pi i}{\omega + \varepsilon_{\mathbf{k}'n'}^{\text{occ}} - \varepsilon_{\mathbf{k}n}^{\text{unocc}} + i\delta}. \end{aligned} \quad (99)$$

Using these results in (92) gives

$$\begin{aligned} P^0(r, r'; \omega) &= - \sum_{\mathbf{k}n}^{\text{occ}} \sum_{\mathbf{k}'n'}^{\text{unocc}} \frac{\phi_{\mathbf{k}n}(r) \phi_{\mathbf{k}n}^*(r') \phi_{\mathbf{k}'n'}(r') \phi_{\mathbf{k}'n'}^*(r)}{\omega + \varepsilon_{\mathbf{k}'n'} - \varepsilon_{\mathbf{k}n} - i\delta} \\ &+ \sum_{\mathbf{k}n}^{\text{unocc}} \sum_{\mathbf{k}'n'}^{\text{occ}} \frac{\phi_{\mathbf{k}n}(r) \phi_{\mathbf{k}n}^*(r') \phi_{\mathbf{k}'n'}(r') \phi_{\mathbf{k}'n'}^*(r)}{\omega + \varepsilon_{\mathbf{k}'n'} - \varepsilon_{\mathbf{k}n} + i\delta} \end{aligned} \quad (100)$$

Interchanging the dummy indices  $\mathbf{k}n \leftrightarrow \mathbf{k}'n'$  in the second term on the right hand side

$$\begin{aligned} P^0(r, r'; \omega) &= \sum_{\mathbf{k}n}^{\text{occ}} \sum_{\mathbf{k}'n'}^{\text{unocc}} \left\{ \frac{\phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r')}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} + i\delta} \right. \\ &\quad \left. - \frac{\phi_{\mathbf{k}n}(r) \phi_{\mathbf{k}'n'}^*(r) \phi_{\mathbf{k}'n'}(r') \phi_{\mathbf{k}n}^*(r')}{\omega + \varepsilon_{\mathbf{k}'n'} - \varepsilon_{\mathbf{k}n} - i\delta} \right\}. \end{aligned} \quad (101)$$

Since  $P^0$  is just the response function of a non-interacting system, we could have used (72), where the many-electron wave functions are single Slater determinants, to obtain the above equation directly. As can be seen the polarisation function satisfies the following symmetry:

$$P(r', r; -\omega) = P(r, r'; \omega). \quad (102)$$

To take into account the spin degree of freedom, we have to multiply the above expression by a factor of two for paramagnetic system. For spin-polarised systems, the above expression is valid for each spin channel and the total  $P^0$  is then the sum of the contribution from each spin channel.

We may rewrite the expression for  $P^0$  as follows.

$$P^0(r, r'; \omega) = \sum_{\mathbf{k}n} \sum_{\mathbf{k}'n'} \left\{ \frac{\phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r')}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} + i\delta} n_{\mathbf{k}n} (1 - n_{\mathbf{k}'n'}) \right. \\ \left. - \frac{\phi_{\mathbf{k}n}(r) \phi_{\mathbf{k}'n'}^*(r) \phi_{\mathbf{k}'n'}(r') \phi_{\mathbf{k}n}^*(r')}{\omega + \varepsilon_{\mathbf{k}'n'} - \varepsilon_{\mathbf{k}n} - i\delta} n_{\mathbf{k}n} (1 - n_{\mathbf{k}'n'}) \right\}. \quad (103)$$

where

$$n_{\mathbf{k}n} = 1 \text{ if } \phi_{\mathbf{k}n} \text{ is occupied} \\ = 0 \text{ if } \phi_{\mathbf{k}n} \text{ is unoccupied.} \quad (104)$$

Interchanging  $\mathbf{k}n \leftrightarrow \mathbf{k}'n'$  in the second term gives

$$P^0(r, r'; \omega) = \sum_{\mathbf{k}n} \sum_{\mathbf{k}'n'} \phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r') \\ \times \left\{ \frac{n_{\mathbf{k}n} (1 - n_{\mathbf{k}'n'})}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} + i\delta} - \frac{n_{\mathbf{k}'n'} (1 - n_{\mathbf{k}n})}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} - i\delta} \right\}. \quad (105)$$

For systems with time reversal symmetry we have for every  $\phi_{\mathbf{k}n}$  a corresponding  $\phi_{-\mathbf{k}n} = \phi_{\mathbf{k}n}^*$  with the same eigenvalue. Therefore

$$P^0(r, r'; \omega) \\ = \frac{1}{2} \sum_{\mathbf{k}n} \sum_{\mathbf{k}'n'} [\phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r') + \phi_{-\mathbf{k}n}^*(r) \phi_{-\mathbf{k}'n'}(r) \phi_{-\mathbf{k}'n'}^*(r') \phi_{-\mathbf{k}n}(r')] \\ \times \left\{ \frac{n_{\mathbf{k}n} (1 - n_{\mathbf{k}'n'})}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} + i\delta} - \frac{n_{\mathbf{k}'n'} (1 - n_{\mathbf{k}n})}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} - i\delta} \right\} \\ = \frac{1}{2} \sum_{\mathbf{k}n} \sum_{\mathbf{k}'n'} [\phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r') + \text{c.c.}] \\ \times \left\{ \frac{n_{\mathbf{k}n} (1 - n_{\mathbf{k}'n'})}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} + i\delta} - \frac{n_{\mathbf{k}'n'} (1 - n_{\mathbf{k}n})}{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n} - i\delta} \right\}. \quad (106)$$

This means we only need to consider the real part of the product of the four wave functions and  $P^0$  is symmetric with respect to an interchange of  $r \leftrightarrow r'$ . Thus  $P^0$  can be written as

$$\text{Re } P^0(r, r'; \omega) = \sum_{\mathbf{k}n} \sum_{\mathbf{k}'n'} \frac{\text{Re}[\phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r')] }{\omega - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n}} (n_{\mathbf{k}n} - n_{\mathbf{k}'n'}) \quad (107)$$

$$\text{Im } P^0(r, r'; \omega) = 2\pi \sum_{\mathbf{k}n}^{\text{occ}} \sum_{\mathbf{k}'n'}^{\text{unocc}} \text{Re}[\phi_{\mathbf{k}n}^*(r) \phi_{\mathbf{k}'n'}(r) \phi_{\mathbf{k}'n'}^*(r') \phi_{\mathbf{k}n}(r')] \delta(|\omega| - \varepsilon_{\mathbf{k}'n'} + \varepsilon_{\mathbf{k}n}) \quad (108)$$

showing that the spectral function is real for systems with time-reversal symmetry.  $P^0$  obeys the following symmetry

$$P^0(r, r'; -\omega) = P^0(r, r'; \omega), \quad (109)$$

$$P^0(r', r; \omega) = P^0(r, r'; \omega), \quad (110)$$

valid for systems with time-reversal symmetry.

## V. PHYSICAL INTERPRETATION OF THE RPA

The underlying physical assumption in the RPA is that the response of an interacting system to a external perturbation is given by the response to the total field (external perturbation plus induced Hartree potential) as if the system is non-interacting. In other words

$$\delta\rho = R\delta\varphi = P^0(\delta\varphi + \delta V_H).$$

Since the change in the Hartree potential is given by

$$\delta V_H = v\delta\rho = vR\delta\varphi$$

we find

$$R\delta\varphi = P^0(\delta\varphi + vR\delta\varphi) = (P^0 + P^0vR)\delta\varphi.$$

Since the perturbing field is arbitrary we conclude that

$$R = P^0 + P^0vR$$

which is the RPA equation.

## VI. THE $GW$ APPROXIMATION

In practice, it is virtually impossible to solve the Hedin equations exactly for real systems. As always, we have to resort to approximations in order to make progress. An approximation to the self-energy due to Hedin which has been found to be very fruitful is the  $GW$  approximation. This approximation may be regarded as an expansion of the self-energy to first order in the screened interaction  $W$  obtained by approximating the vertex in (49) by

$$\Lambda(1, 2, 3) = \delta(1 - 2)\delta(1 - 3), \quad (111)$$

neglecting the self-energy response to the total field  $\delta\Sigma/\delta V$ . With this approximation the self-energy becomes

$$\Sigma(1, 2) = iG(1, 2)W(2, 1), \quad (112)$$

hence the name  $GW$  approximation. For systems with time reversal symmetry (without magnetic field)  $W(1, 2) = W(2, 1)$ . The polarisation function becomes

$$P(1, 2) = -iG(1, 2)G(2, 1^+). \quad (113)$$

The screened interaction is calculated from (51) with  $P$  approximated by  $P^0$ .

$$W(1, 2) = v(1 - 2) + \int d3d4 v(1 - 3)P^0(3, 4)W(4, 2). \quad (114)$$

In frequency space the self-energy in the GWA is given by

$$\Sigma(r, r'; \omega) = i \int \frac{d\omega'}{2\pi} G(r, r'; \omega + \omega')W(r', r; \omega') \quad (115)$$

which follows from the convolution theorem of the Fourier transform. The self-energy consists of the exchange and correlation parts. The exchange part is given by

$$\Sigma^x(r, r'; \omega) = i \int \frac{d\omega'}{2\pi} G(r, r'; \omega + \omega')v(r - r')e^{i\eta\omega'}. \quad (116)$$

The converging factor  $\exp(i\eta\omega')$  arises from the rule that equal time Green's function should be taken as  $G(rt, r't^+)$ . Using the spectral representation of  $G$  in (117) we obtain

$$G(r, r'; \omega) = \int_{-\infty}^{\mu} d\omega' \frac{A(r, r'; \omega')}{\omega - \omega' - i\delta} + \int_{\mu}^{\infty} d\omega' \frac{A(r, r'; \omega')}{\omega - \omega' + i\delta}. \quad (117)$$

$$\begin{aligned}
\Sigma^x(r, r'; \omega) &= iv(r - r') \int \frac{d\omega'}{2\pi} \\
&\times \left\{ \int_{-\infty}^{\mu} d\omega_1 \frac{A(r, r'; \omega_1)}{\omega + \omega' - \omega_1 - i\delta} + \int_{\mu}^{\infty} d\omega_1 \frac{A(r, r'; \omega_1)}{\omega + \omega' - \omega_1 + i\delta} \right\} e^{i\eta\omega'} \\
&= -v(r - r') \int_{-\infty}^{\mu} d\omega_1 A(r, r'; \omega_1).
\end{aligned} \tag{118}$$

Due to the converging factor  $\exp(i\eta\omega')$  the contour can be closed in the upper-half circle and only the first term in the bracket contributes. If we replace the spectral function  $A$  by a non-interacting one

$$A^0(r, r'; \omega) = \sum_n \phi_n(r) \phi_n^*(r') \delta(\omega - \varepsilon_n) \tag{119}$$

we find the familiar expression of the Fock exchange.

$$\Sigma^x(r, r') = -v(r - r') \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') \tag{120}$$

As for the response function, the correlation part of the screened interaction defined by

$$W^c = W - v \tag{121}$$

can be written in terms of its spectral representation because from (47)

$$W^c = vRv \tag{122}$$

so that the frequency dependence of  $W^c$  is determined by the response function  $R$ . Thus,

$$\begin{aligned}
W^c(r, r'; \omega) &= \int_{-\infty}^0 d\omega' \frac{D(r, r'; \omega')}{\omega - \omega' - i\eta} + \int_0^{\infty} d\omega' \frac{D(r, r'; \omega')}{\omega - \omega' + i\eta} \\
&= \int_0^{\infty} d\omega' D(r, r'; \omega') \left\{ \frac{1}{\omega - \omega' + i\eta} - \frac{1}{\omega + \omega' - i\eta} \right\}.
\end{aligned} \tag{123}$$

Like the response function  $R$  the symmetry property of  $W^c$  is given by

$$W^c(r', r; -\omega) = W^c(r, r'; \omega) \tag{124}$$

and the spectral function has the following symmetry

$$D(r, r'; -\omega) = -D(r, r'; \omega). \tag{125}$$

For systems with time-reversal symmetry

$$D(r', r; \omega) = D(r, r'; \omega). \tag{126}$$

Using the spectral representation of  $G$  in (117) and the above spectral representation for  $W^c$  the self-energy consists of four integrals but only two survive.

$$\begin{aligned}
\Sigma^c(r, r'; \omega) &= i \int \frac{d\omega'}{2\pi} \int_{-\infty}^{\mu} d\omega_1 \int_0^{\infty} d\omega_2 \frac{A(r, r'; \omega_1)}{\omega + \omega' - \omega_1 - i\delta} \times \frac{D(r', r; \omega_2)}{\omega' - \omega_2 + i\eta} \\
&\quad - i \int \frac{d\omega'}{2\pi} \int_{\mu}^{\infty} d\omega_1 \int_0^{\infty} d\omega_2 \frac{A(r, r'; \omega_1)}{\omega + \omega' - \omega_1 + i\delta} \times \frac{D(r', r; \omega_2)}{\omega' + \omega_2 - i\eta} \\
&= \int_{-\infty}^{\mu} d\omega_1 \int_0^{\infty} d\omega_2 \frac{A(r, r'; \omega_1) D(r', r; \omega_2)}{\omega + \omega_2 - \omega_1 - i\delta} \\
&\quad + \int_{\mu}^{\infty} d\omega_1 \int_0^{\infty} d\omega_2 \frac{A(r, r'; \omega_1) D(r', r; \omega_2)}{\omega - \omega_2 - \omega_1 + i\delta} \\
&= \int_{-\infty}^{\infty} d\omega_1 \theta(\mu - \omega_1) \int_{-\infty}^{\infty} d\omega_2 \theta(\omega_2) \frac{A(r, r'; \omega_1) D(r', r; \omega_2)}{\omega + \omega_2 - \omega_1 - i\delta} \\
&\quad + \int_{-\infty}^{\infty} d\omega_1 \theta(\omega_1 - \mu) \int_{-\infty}^{\infty} d\omega_2 \theta(\omega_2) \frac{A(r, r'; \omega_1) D(r', r; \omega_2)}{\omega - \omega_2 - \omega_1 + i\delta}. \tag{127}
\end{aligned}$$

The correlation part of the self-energy can also be written as a spectral representation.

$$\Sigma^c(r, r'; \omega) = \int_{-\infty}^{\mu} d\omega_1 \frac{\Gamma(r, r'; \omega_1)}{\omega - \omega_1 - i\delta} + \int_{\mu}^{\infty} d\omega_1 \frac{\Gamma(r, r'; \omega_1)}{\omega - \omega_1 + i\delta} \tag{128}$$

where

$$\Gamma(r, r'; \omega) = -\frac{1}{\pi} \text{sgn}(\omega - \mu) \text{Im} \Sigma^c(r, r'; \omega). \tag{129}$$

Approximating the spectral function  $A$  by its non-interacting value

$$A^0(r, r'; \omega) = \sum_n \phi_n(r) \phi_n^*(r') \delta(\omega - \varepsilon_n) \tag{130}$$

we obtain

$$\begin{aligned}
\Sigma^c(r, r'; \omega) &= \sum_n \theta(\mu - \varepsilon_n) \int_{-\infty}^{\infty} d\omega_2 \theta(\omega_2) \frac{\phi_n(r) \phi_n^*(r') D(r', r; \omega_2)}{\omega + \omega_2 - \varepsilon_n - i\delta} \\
&\quad + \sum_n \theta(\varepsilon_n - \mu) \int_{-\infty}^{\infty} d\omega_2 \theta(\omega_2) \frac{\phi_n(r) \phi_n^*(r') D(r', r; \omega_2)}{\omega - \omega_2 - \varepsilon_n + i\delta} \tag{131}
\end{aligned}$$

so that

$$\Gamma(r, r'; \omega \leq \mu) = \sum_n^{\text{occ}} \theta(\varepsilon_n - \omega) \phi_n(r) \phi_n^*(r') D(r', r; \varepsilon_n - \omega), \tag{132}$$

$$\Gamma(r, r'; \omega > \mu) = \sum_n^{\text{unocc}} \theta(\omega - \varepsilon_n) \phi_n(r) \phi_n^*(r') D(r', r; \omega - \varepsilon_n) \tag{133}$$

The real part of the correlation part of the self-energy is obtained from the Hilbert transform

$$\text{Re} \Sigma^c(r, r'; \omega) = P \int_{-\infty}^{\infty} d\omega' \frac{\Gamma(r, r'; \omega')}{\omega - \omega'}, \tag{134}$$

which is a principal value integral.



### A. The screened exchange and Coulomb hole

The real part of the self-energy expression in the GWA can be rewritten in a more physically transparent form.

$$\begin{aligned}
\text{Re } \Sigma^c(r, r'; \omega) &= \sum_n \theta(\mu - \varepsilon_n) \int_{-\infty}^{\infty} d\omega_2 \theta(\omega_2) \frac{\phi_n(r) \phi_n^*(r') D(r', r; \omega_2)}{\omega + \omega_2 - \varepsilon_n} \\
&+ \sum_n \theta(\varepsilon_n - \mu) \int_{-\infty}^{\infty} d\omega_2 \theta(\omega_2) \frac{\phi_n(r) \phi_n^*(r') D(r', r; \omega_2)}{\omega - \omega_2 - \varepsilon_n} \\
&= \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') \int_{-\infty}^{\infty} d\omega_2 \frac{D(r', r; \omega_2)}{\omega + \omega_2 - \varepsilon_n} \\
&- \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') \int_{-\infty}^0 d\omega_2 \frac{D(r', r; \omega_2)}{\omega + \omega_2 - \varepsilon_n} \\
&+ \sum_n^{\text{unocc}} \phi_n(r) \phi_n^*(r') \int_0^{\infty} d\omega_2 \frac{D(r', r; \omega_2)}{\omega - \omega_2 - \varepsilon_n} \\
&= - \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') W^c(r', r; \varepsilon_n - \omega) \\
&+ \sum_n \phi_n(r) \phi_n^*(r') \int_0^{\infty} d\omega_2 \frac{D(r', r; \omega_2)}{\omega - \omega_2 - \varepsilon_n} \tag{135}
\end{aligned}$$

Combining with the exchange part yields

$$\begin{aligned}
\text{Re } \Sigma(r, r'; \omega) &= - \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') W(r', r; \varepsilon_n - \omega) \\
&+ \sum_n \phi_n(r) \phi_n^*(r') \int_0^{\infty} d\omega_2 \frac{D(r', r; \omega_2)}{\omega - \omega_2 - \varepsilon_n}. \tag{136}
\end{aligned}$$

The first term has a clear meaning of screened exchange. It has the same form as the bare exchange except that in place of the bare Coulomb interaction  $v$  we have instead the screened interaction  $W$ . The second term is called the Coulomb hole term and its meaning becomes clear when we make an approximation  $\omega - \varepsilon_n \approx 0$  which results in

$$\begin{aligned}
\text{Re } \Sigma(r, r'; \omega) &= - \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') W(r', r; 0) + \sum_n \phi_n(r) \phi_n^*(r') W^c(r, r'; 0) \\
&= - \sum_n^{\text{occ}} \phi_n(r) \phi_n^*(r') W(r', r; 0) + \frac{1}{2} \delta(r - r') W^c(r, r'; 0). \tag{137}
\end{aligned}$$

This approximation, due to Hedin, is known as the COHSEX (Coulomb hole and screened exchange) approximation. The Coulomb hole term may be interpreted as the interaction

between an electron and its screening Coulomb hole charge. The factor of one half is due to the adiabatic switching of the interaction from zero to  $W^c(0)$ . Note that  $W^c(0)$  is generally negative, in agreement with the interpretation of interaction between an electron and its screening hole.

## VII. QUASIPARTICLE

For finite systems such as atoms and molecules, the eigen energies are discrete and we need not introduce a chemical potential  $\mu$ . However, as the system approaches the thermodynamic limit ( $N \rightarrow \infty$ ,  $\Omega \rightarrow \infty$ ) the eigen energies becomes continuous and it does not make sense anymore to speak about an individual discrete eigen energy. In particular for metals the chemical potential is essential to distinguish occupied from unoccupied states.

To illustrate the structure of the Green function consider for example a periodic crystal. Let us first start with a non-interacting Green's function constructed from a set of one-particle eigenstates which may be taken to be those of the Kohn-Sham eigenstates:

$$\left[ -\frac{1}{2}\nabla^2 + V_{KS}(r) \right] \phi_{\mathbf{k}m}(r) = \varepsilon_{\mathbf{k}m} \phi_{\mathbf{k}m}(r). \quad (138)$$

$\mathbf{k}$  labels the Bloch wave vector and  $n$  labels the band index. To construct the Green function we must calculate  $\langle N-1, n | \hat{\psi}(r) | \Psi \rangle$ . The field operator for a crystal is given by

$$\hat{\psi}(r) = \sum_{\mathbf{k}m} \phi_{\mathbf{k}m}(r) \hat{c}_{\mathbf{k}m} \quad (139)$$

$$\langle N-1, n | \hat{\psi}(r) | \Psi \rangle = \sum_{\mathbf{k}m} \phi_{\mathbf{k}m}(r) \langle N-1, n | \hat{c}_{\mathbf{k}m} | \Psi \rangle. \quad (140)$$

The Kohn-Sham ground state is a Slater determinant corresponding to the lowest filled Kohn-Sham eigenstates. For a non-zero matrix element, the  $N-1$  excited state  $|N-1, n\rangle$  must be the ground state  $|0\rangle$  with one orbital empty, say  $\phi_{\mathbf{k}n}$ . Similarly

$$\langle N+1, n | \psi^+(r) | \Psi \rangle = \sum_{\mathbf{k}m} \phi_{\mathbf{k}m}^*(r) \langle N+1, n | \hat{c}_{\mathbf{k}m}^+ | \Psi \rangle \quad (141)$$

is non-zero when the  $N+1$  excited state  $|N+1, n\rangle$  is the ground state with an extra electron occupying an unoccupied orbital, say  $\phi_{\mathbf{k}n}$ . The non-interacting spectral function is therefore given by

$$A^0(r, r'; \omega) = \sum_{\mathbf{k}n} \phi_{\mathbf{k}n}(r) \phi_{\mathbf{k}n}^*(r') \delta(\omega - \varepsilon_{\mathbf{k}n}), \quad (142)$$

where the sum is over all orbitals, occupied and unoccupied. We have measured the one-particle excitation energies  $\varepsilon_{\mathbf{k}n}$  with respect to the chemical potential, as often done in practice. The non-interacting Green's function is then

$$G^0(r, r'; \omega) = \sum_{\mathbf{k}n}^{\text{occ}} \frac{\phi_{\mathbf{k}n}(r)\phi_{\mathbf{k}n}^*(r')}{\omega - \varepsilon_{\mathbf{k}n} - i\delta} + \sum_{\mathbf{k}n}^{\text{unocc}} \frac{\phi_{\mathbf{k}n}(r)\phi_{\mathbf{k}n}^*(r')}{\omega - \varepsilon_{\mathbf{k}n} + i\delta}. \quad (143)$$

The occupied part is referred to as the hole Green's function and the unoccupied part the particle or electron Green's function.

Let us now turn on the interaction and consider the spectral function.

$$\begin{aligned} A(r, r'; \omega) &= \sum_n \langle \Psi | \psi^+(r') | N-1, n \rangle \langle N-1, n | \psi(r) | \Psi \rangle \delta(\omega - \mu + \Delta_n(N-1)) \\ &+ \sum_n \langle \Psi | \psi(r) | N+1, n \rangle \langle N+1, n | \psi^+(r') | \Psi \rangle \delta(\omega - \mu - \Delta_n(N+1)) \end{aligned} \quad (144)$$

where

$$\varepsilon_n = \begin{cases} E_n(N+1) - E_0 = \Delta_n(N+1) + \mu, & \text{unoccupied} \\ -(E_n(N-1) - E_0) = -\Delta_n(N-1) + \mu, & \text{occupied} \end{cases}.$$

The  $N \pm 1$ -particle eigenstates  $|n\rangle$  as well as the ground state  $|\Psi\rangle$  are no longer single Slater determinants, but rather linear combinations of Slater determinants.

$$\begin{aligned} \langle N+1, n | \psi^+(r) | \Psi \rangle &= \sum_{\mathbf{k}m} \phi_{\mathbf{k}m}^*(r) \langle N+1, n | \hat{c}_{\mathbf{k}m}^+ | \Psi \rangle \\ &= \sum_{\mathbf{k}m, \alpha\alpha'} \phi_{\mathbf{k}m}^*(r) b_{\alpha}^{n*} \langle N+1, \alpha | \hat{c}_{\mathbf{k}m}^+ | N, \alpha' \rangle b_{\alpha'}^0 \\ &= \sum_{\mathbf{k}m} \phi_{\mathbf{k}m}^*(r) b_{\mathbf{k}m}^{(N+1, n)*} \end{aligned} \quad (145)$$

where  $|N \pm 1, \alpha\rangle$  are Slater determinants with  $N \pm 1$  particles and we have expanded the  $N \pm 1$ -particle eigenstates as linear combinations of Slater determinants  $|N \pm 1, \alpha\rangle$ .

$$|N \pm 1, n\rangle = \sum_{\alpha} |N \pm 1, \alpha\rangle b_{\alpha}^n. \quad (146)$$

We have defined

$$\begin{aligned} b_{\mathbf{k}m}^{(N+1, n)*} &= \sum_{\alpha\alpha'} b_{\alpha}^{n*} \langle N+1, \alpha | \hat{c}_{\mathbf{k}m}^+ | N, \alpha' \rangle b_{\alpha'}^0 \\ &= \langle N+1, n | \hat{c}_{\mathbf{k}m}^+ | \Psi \rangle \end{aligned} \quad (147)$$

We obtain

$$\begin{aligned}
A(r, r'; \omega) &= \sum_n \sum_{\mathbf{k}mm'} \phi_{\mathbf{k}m}(r) \phi_{\mathbf{k}m'}^*(r') b_{\mathbf{k}m}^{(N-1,n)} b_{\mathbf{k}m'}^{(N-1,n)*} \delta(\omega - \mu + \Delta_n(N-1)) \\
&+ \sum_n \sum_{\mathbf{k}mm'} \phi_{\mathbf{k}m}(r) \phi_{\mathbf{k}m'}^*(r') b_{\mathbf{k}m}^{(N+1,n)} b_{\mathbf{k}m'}^{(N+1,n)*} \delta(\omega - \mu - \Delta_n(N+1)). \quad (148)
\end{aligned}$$

Taking a matrix element in an orbital  $\phi_{\mathbf{k}l}$  yields

$$\begin{aligned}
A_{\mathbf{k}l}(\omega) &= \sum_n \left| b_{\mathbf{k}l}^{(N-1,n)} \right|^2 \delta(\omega - \mu + \Delta_n(N-1)) \\
&+ \sum_n \left| b_{\mathbf{k}l}^{(N+1,n)} \right|^2 \delta(\omega - \mu - \Delta_n(N+1)). \quad (149)
\end{aligned}$$

For a non-interacting system there is only one contribution from the sum over  $n$  of the  $N \pm 1$ -particle excited states and the corresponding weight  $|b_{\mathbf{k}l}^{(N \pm 1, n)}|^2$  is unity. For an interacting system, in general the states  $n$  become continuous and they contribute to the spectral function with varying weights resulting in the  $\delta$ -function becoming a broadened peak. The width of the peak is inversely proportional to the life time of the quasiparticle. In the non-interacting system, the quasiparticle is a  $\delta$ -function with zero width or infinite life time because it is an eigenstate of the system. There is no interaction that causes the quasiparticle to decay to other states. In an interacting system, the quasiparticle is no longer in general an eigenstate of the system and it can therefore decay to other states due to its interactions with other quasiparticles and excitations of the system.

Even if  $\phi_{\mathbf{k}l}$  is an occupied orbital in the non-interacting system,  $A_{\mathbf{k}l}(\omega)$  in general has weight above the Fermi level, as can be seen in (149). Conversely, when  $\phi_{\mathbf{k}l}$  is an unoccupied orbital in the non-interacting system,  $A_{\mathbf{k}l}(\omega)$  in general has weight below the Fermi level. Note that independent of whether the system is interacting or not

$$\int d\omega A_{\mathbf{k}l}(\omega) = 1 \quad (150)$$

and the total spectral function is given by the trace

$$\sum_{\mathbf{k}l} \int d\omega A_{\mathbf{k}l}(\omega) = N \quad (151)$$

where  $N$  is the total number of electrons. The trace is independent of the choice of the orbitals.

It is not *apriori* obvious but it turns out that in many materials, the spectral function  $A_{\mathbf{k}l}(\omega)$  is peaked at a certain energy  $E_{\mathbf{k}l}$  which may be shifted from the non-interacting  $\delta$ -function peak at the non-interacting orbital energy  $\varepsilon_{\mathbf{k}l}$ . This main peak which may be traced back to the peak of the non-interacting system is referred to as "quasiparticle peak" with weight less than unity. In addition, there may be additional peaks at different energies which are not present in the non-interacting system. These additional peaks are called "satellite peaks" which may arise from the coupling between electrons and plasmons. There are also atomic-like satellites. As a rule of thumb one may say that the lesser the quasiparticle weight from unity the stronger the correlations. Evidently, the closer the quasiparticle weight to unity the better a one-particle approximation should be. In some materials, the quasiparticle peak may disappear or become very small and these materials are called strongly correlated materials. A one-particle approximation would not provide a satisfactory description in this case and one must take into account the many-body effects or correlation effects to describe the spectral function.

We can also understand the concept of quasiparticle from the self-energy point of view. From the Dyson equation we have

$$G(\omega) = G^0(\omega) + G^0(\omega)\Sigma(\omega)G(\omega). \quad (152)$$

Solving for  $G$  we obtain a matrix equation

$$G(\omega) = [1 - G^0(\omega)\Sigma(\omega)]^{-1}G^0(\omega) \quad (153)$$

which can be solved in some chosen basis functions. Taking the matrix element with respect to an orbital  $\phi_{\mathbf{k}n}$  and *assuming* that the self-energy is diagonal in the orbital basis  $\{\phi_{\mathbf{k}n}\}$  we obtain

$$\begin{aligned} G_{\mathbf{k}n}(\omega) &= \frac{G_{\mathbf{k}n}^0(\omega)}{1 - G_{\mathbf{k}n}^0(\omega)\Sigma_{\mathbf{k}n}(\omega)} \\ &= \frac{1}{(G^0)^{-1}_{\mathbf{k}n}(\omega) - \Sigma_{\mathbf{k}n}(\omega)} \\ &= \frac{1}{\omega - \varepsilon_{\mathbf{k}n} - \Sigma_{\mathbf{k}n}(\omega)}. \end{aligned} \quad (154)$$

We have

$$(G^0)^{-1}_{\mathbf{k}n}(\omega) = \omega - \varepsilon_{\mathbf{k}n}, \quad (155)$$

since  $\phi_{\mathbf{k}n}$  is an eigenfunction of  $\hat{h}$  with eigenvalue  $\varepsilon_{\mathbf{k}n}$ . Taking the imaginary part of  $G_{\mathbf{k}n}$ , which is proportional to the spectral function, gives

$$\text{Im } G_{\mathbf{k}n}(\omega) = \frac{\text{Im } \Sigma_{\mathbf{k}n}(\omega)}{[\omega - \varepsilon_{\mathbf{k}n} - \text{Re } \Sigma_{\mathbf{k}n}(\omega)]^2 + [\text{Im } \Sigma_{\mathbf{k}n}(\omega)]^2}. \quad (156)$$

At a certain  $\omega$  we may find that

$$\omega - \varepsilon_{\mathbf{k}n} - \text{Re } \Sigma_{\mathbf{k}n}(\omega) = 0 \quad (157)$$

and we refer to the solution to this equation as the quasiparticle energy.

$$E_{\mathbf{k}n} = \varepsilon_{\mathbf{k}n} + \text{Re } \Sigma_{\mathbf{k}n}(E_{\mathbf{k}n}). \quad (158)$$

At that energy

$$\text{Im } G_{\mathbf{k}n}(E_{\mathbf{k}n}) = \frac{1}{\text{Im } \Sigma_{\mathbf{k}n}(E_{\mathbf{k}n})}. \quad (159)$$

It is not *a priori* clear but in many materials  $\text{Im } \Sigma_{\mathbf{k}n}(E_{\mathbf{k}n})$  is small so that  $\text{Im } G_{\mathbf{k}n}(\omega)$  exhibits a peak at  $\omega \approx E_{\mathbf{k}n}$ . This peak is referred to as a quasiparticle peak. Thus,  $\text{Im } G_{\mathbf{k}n}(\omega)$  is no longer a  $\delta$ -function centred at  $\omega = \varepsilon_{\mathbf{k}n}$  but rather a Lorentzian centred at  $E_{\mathbf{k}n} = \varepsilon_{\mathbf{k}n} + \text{Re } \Sigma_{\mathbf{k}n}(E_{\mathbf{k}n})$ . The quasiparticle peak is shifted from the non-interacting value by the self-energy shift  $\text{Re } \Sigma_{\mathbf{k}n}(E_{\mathbf{k}n})$ . The width of the quasiparticle peak is given by  $\text{Im } \Sigma_{\mathbf{k}n}(E_{\mathbf{k}n})$  which represents the *inverse* life time of the quasiparticle. The narrower the peak the longer the life time and this becomes infinite (zero width) in the non-interacting case since the quasiparticle becomes an eigenstate of the system. The self-energy has two main effects on the non-interacting quasiparticle peak: it shifts and broadens the peak.

## VIII. APPENDICES

### A. The Heisenberg and Dirac pictures

Requiring that matrix elements of an operator be independent of pictures we have

$$\langle \Psi_H | \hat{O}_H(t) | \Psi_H \rangle = \langle \Psi_D(t) | \hat{O}_D(t) | \Psi_D(t) \rangle. \quad (160)$$

The state in the Heisenberg picture is independent of time whereas the state in the Dirac (interaction) picture develops according to

$$|\Psi_D(t)\rangle = \hat{U}(t, t') |\Psi_D(t')\rangle. \quad (161)$$

Since by convention both states coincide at  $t = 0$  we find

$$\begin{aligned} \langle \Psi_H | \hat{O}_H(t) | \Psi_H \rangle &= \langle \Psi_D(0) | \hat{U}(0, t) \hat{O}_D(t) \hat{U}(t, 0) | \Psi_D(0) \rangle \\ &= \langle \Psi_H | \hat{U}(0, t) \hat{O}_D(t) \hat{U}(t, 0) | \Psi_H \rangle \end{aligned} \quad (162)$$

and conclude that

$$\hat{O}_H(t) = \hat{U}(0, t) \hat{O}_D(t) \hat{U}(t, 0). \quad (163)$$

## B. Equal-time Green function

Equal-time Green function originates from the Coulomb interaction being instantaneous in the non-relativistic treatment. Consider the Coulomb interaction term of the many-electron Hamiltonian:

$$\hat{V} = \frac{1}{2} \int dr dr' \hat{\psi}^\dagger(r) \hat{\psi}^\dagger(r') v(r - r') \hat{\psi}(r') \hat{\psi}(r). \quad (164)$$

Multiplying by  $\exp(iHt)$  on the left and by  $\exp(-iHt)$  on the right and inserting  $\exp(-iHt) \exp(iHt)$  in between pairs of field operators we find in the Heisenberg representation

$$\hat{V}(t) = \frac{1}{2} \int dr dr' \hat{\psi}_H^\dagger(rt) \hat{\psi}_H^\dagger(r't) v(r - r') \hat{\psi}_H(r't) \hat{\psi}_H(rt). \quad (165)$$

Consider the Hartree and exchange terms arising from this interaction term:

$$\begin{aligned} \hat{V}(t) &= \int dr dr' \hat{\psi}_H^\dagger(rt) \langle \hat{\psi}_H^\dagger(r't) \hat{\psi}_H(r't) \rangle v(r - r') \hat{\psi}_H(rt) \quad (\text{Hartree}) \\ &\quad - \int dr dr' \hat{\psi}_H^\dagger(r't) \langle \hat{\psi}_H^\dagger(rt) \hat{\psi}_H(r't) \rangle v(r - r') \hat{\psi}_H(rt) \quad (\text{exchange}) \end{aligned} \quad (166)$$

where

$$\begin{aligned} \langle \hat{\psi}_H^\dagger(r't) \hat{\psi}_H(r't) \rangle &= \langle \Psi | \hat{\psi}_H^\dagger(r't) \hat{\psi}_H(r't) | \Psi \rangle \\ &= -iG(r't, r't^+), \end{aligned} \quad (167)$$

$$\begin{aligned}
\langle \hat{\psi}_H^\dagger(rt) \hat{\psi}_H(r't) \rangle &= \langle \Psi | \hat{\psi}_H^\dagger(rt) \hat{\psi}_H(r't) | \Psi \rangle \\
&= -iG(rt, r't^+).
\end{aligned}
\tag{168}$$

Thus we see that Hartree and Fock exchange terms can be written in terms of equal-time Green function and to get the right ordering of the field operators, equal-time ( $t' = t$ ) Green function must be interpreted as

$$G(rt, r't') \rightarrow G(rt, r't^+). \tag{169}$$

This interpretation also holds when we consider a perturbation expansion of the Green function in powers of the Coulomb interaction and the non-interacting Green function in Wick's theorem.

The Fourier transform is defined according to

$$G(\omega) = \int d\tau e^{i\omega\tau} G(\tau),$$

$$G(\tau) = \int \frac{d\omega}{2\pi} e^{-i\omega\tau} G(\omega).$$

We then have with  $\tau = t - t' = -\eta$

$$G(rt, r't^+) = G(r, r'; \tau) = \int \frac{d\omega}{2\pi} e^{i\omega\eta} G(\omega).$$

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[1] L. Hedin, Phys. Rev. **139** A796 (1965); L. Hedin and S. Lundqvist in *Solid State Physics* Vol. 23, F. Seits, D. Turnbull and H. Ehrenreich, Eds. (Academic Press, New York, 1969)