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DERIVATION OF AN EXPRESSION FOR THE ENERGY GAP IN A SEMICONDUCTOR

by

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Abstract

The Kohn-Sham density-functional equations providing the exact groundstate density for a given many-electron system do not lead to a correct value for the energy gap in a semiconductor. A rederivation is given of an expression, obtained earlier by Perdew and Levy and Sham and Schlüter, which yields the correction to the Kohn-Sham energy gap. This correction is due to a discontinuity in the exchange-correlation functional. It can be expressed in terms of a mass operator which is related to those electron-electron interactions not yet accounted for in the Kohn-Sham description of groundstate properties. The main reason for the present derivation is to elucidate the role of the various concepts and arguments that finally lead to the gap correction.

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1. Introduction

The derivation of a first-principle expression for the energy gap in a semiconductor requires a careful incorporation of electron-electron interaction effects. In approximate schemes such as Hartree-, Hartree-Fock[1], or Hohenberg-Kohn[2,3] (HK) (local) density functional (LDF)-approach drastically different values for the energy gap result, indicating at least that there is a serious problem. In what follows we shall take the LDF-theory as a starting point. Within this theory a (wrong) energy gap is obtained[4-9], but it will turn out that a correction term can be derived, which leads to the true energy gap.

It is well known that the one-particle Kohn-Sham (KS)-equations[9] play a central role in LDF-theory. For a semiconductor they lead to a gap in the one-particle spectrum. This gap is equal to the difference between the lowest "unoccupied" and the highest "occupied" single-particle Kohn-Sham energy level. In deriving an expression for the correction to this KS-gap, it turns out that an important role is played by a *discontinuity* in the *functional derivative*[4,8] of the exchange-correlation functional (which is part of the total energy functional in the HK-theory). For a short introduction to the theory of functional derivative as well as for a compendium of useful differentiation rules the reader is referred to Appendix A. The above-mentioned discontinuity can be shown to be expressiable in terms of many-body energy corrections, which, in principle, can be calculated. Practical schemes in order to achieve this, will have to be developed if a definite value for the energy gap is to be obtained.

2. Noninteracting system

Let us first consider a hypothetical system of non-interacting electrons in a semiconducting crystal. This case is instructive, since it demonstrates that the functional derivative of the *kinetic* energy, when regarded as a functional of the density, exhibits a discontinuity which is related to the existence of an energy gap. More generally, in *real* systems it will be shown later on that the discontinuity in the functional derivative of both the kinetic and the exchange-correlation-energy functional are related to the energy gap.

In the absence of electron-electron interactions, the total energy as a functional of the electron density can be written in the form[9]

$$E_u[\rho] = \int d^3r\, u(\underline{r})\, \rho(\underline{r}) + K[\rho]. \qquad (2.1)$$

Here, $\rho(\underline{r})$ is the density of electrons, $u(\underline{r})$ is the static external potential due to the ions in the crystal and $K[\rho]$ is the kinetic-energy functional. Even for a system of noninteracting electrons, the explicit form of K as a functional of ρ is not known, although more or less satisfactory approximations are available[2,3,9].

If electron-electron interactions would be taken into account, then the missing terms in (2.1) are the Hartree- and exchange-correlation energy contributions. These terms will be introduced in section 3.

Let us consider a finite system with a given external potential (i.e. due to the ions). Bij N we shall denote the number of electrons for which the system is charge neutral. In the case of a semiconductor in the ground-state this number N is reached when all valence (conduction) bands are completely filled (empty). The number M will be used to indicate a more or less hypothetical situation in which a certain number of electrons have been added to or removed from the charge-neutral crystal, while keeping the ion potential unchanged; that is, letting the ions stay at their fixed positions. We always think of M as a number relatively close to N, $M = N \pm n$, where n is usually of order 1 (note that N is of order of 10^{23} or so). Sometimes we shall also consider N and M as variable quantities which can approach infinitely large values. In such cases, we explicitly mean a limiting procedure in which the crystal volume Ω tends to infinity,

without changing the bulk properties of the ionic potential, while both N and M tend to infinity in such a way that the concentration N/Ω is constant.

The Hohenberg-Kohn theorem[2] asserts that the ground-state density $\rho(\underline{r})$, under the subsidiary condition

$$\int d^3r\, \rho(\underline{r}) = M, \tag{2.2}$$

can be found by minimizing the total energy (2.1), that is by solving

$$\delta \{E_u[\rho] - \mu_M \int d^3r\, \rho(\underline{r})\} = 0. \tag{2.3}$$

Here, the chemical potential μ_M appears as a Lagrange multiplier, to be determined from (2.2). According to (2.3) and (2.1), the M-electron ground-state density satisfies the equation

$$\frac{\delta E_u[\rho]}{\delta \rho} = \frac{\delta K[\rho]}{\delta \rho} + u(\underline{r}) = \mu_M. \tag{2.4}$$

Although $K[\rho]$ is not known in an explicit form, eq. (2.4) can nevertheless be solved. Namely, in this special case one can calculate $\rho(\underline{r})$ by first finding the solutions $\psi_j(\underline{r})$ of

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + u(\underline{r})\right]\psi_j(\underline{r}) = \varepsilon_j\,\psi_j(\underline{r}), \quad j = 1,2,3,\ldots, \tag{2.5}$$

where it is assumed that the eigenenergies ε_j satisfy $\varepsilon_{j+1} \geq \varepsilon_j$ for all j. The corresponding wave functions $\{\psi_j(\underline{r})\}$ form a complete orthonormal set of functions, and the density can be expressed in terms of the $\psi_j(\underline{r})$-functions which correspond to the lowest M eigenenergies, or,

$$\rho_M(\underline{r}) = \sum_{j=1}^{M} |\psi_j(\underline{r})|^2. \tag{2.6}$$

The kinetic energy $K[\rho_M]$ can now be expressed as

$$K[\rho_M] = \sum_{j=1}^{M} \int d^3r\, \psi^*_j(\underline{r})\left(\frac{-\hbar^2}{2m}\nabla^2\right)\psi_j(\underline{r}). \tag{2.7}$$

Eq. (2.7) can also be interpreted as to define the functional K of ρ. Namely, the ψ_j's can be considered as functionals of an external potential, which in turn, according to Hohenberg-Kohn theorem[2], is an unique functional of $\rho(\underline{r})$ (apart from a trivial additive constant).

Let us now demonstrate the origin of the discontinuity. For $M \neq N$, it is well known that the chemical potential for a non-interacting semiconducting system with M electrons in the ground state must be identified with the energy level ε_M in (2.5), or

$$\mu_M = \varepsilon_M, \quad M \neq N. \tag{2.8}$$

Note that, for sufficiently large crystal volume, the $\{\varepsilon_M\}$ can be regarded as a continuum of eigenvalues except across the gap. Hence, the discontinuity in ε_M occurs when M changes from N to N+1. More specifically, the situation with precise N electrons is very special in the following sense: In the state with M electrons, the removal of one electron lowers the total energy by ε_M while the addition of one electron raises the total energy by ε_{M+1}. For all $M \neq N$, the difference between ε_{M+1} and ε_M is infinitesimally small, but for $M = N$ these quantities differ by the band gap energy.

The gap energy E_g in our noninteracting model system is simply equal to this discontinuity, or

$$E_g = \varepsilon_{N+1} - \varepsilon_N. \tag{2.9}$$

By applying (2.4) and (2.8) for different values of M, namely M = N+1 and M = N-1, while the potential $u(\underline{r})$ is kept unchanged, we obtain†)

$$\left.\frac{\delta K[\rho_M]}{\delta \rho(\underline{r})}\right|_{\rho=\rho_{N+1}} + u(\underline{r}) = \varepsilon_{N+1}, \tag{2.10a}$$

$$\left.\frac{\delta K[\rho_M]}{\delta \rho(\underline{r})}\right|_{\rho=\rho_{N-1}} + u(\underline{r}) = \varepsilon_{N-1}. \tag{2.10b}$$

†) Note that we avoid to differentiate at $\rho(\underline{r}) = \rho_N(\underline{r})$, since the derivative is an ill-defined quantity there.

Subtracting (2.10b) from (2.10a), and recalling that for sufficient large volume Ω we can put $\varepsilon_{N+1} - \varepsilon_{N-1}$ equal to E_g, we find

$$E_g = \frac{\delta K}{\delta_+ \rho(\underline{r})} - \frac{\delta K}{\delta_- \rho(\underline{r})} \quad , \tag{2.11}$$

where we have introduced a short-hand notation by defining

$$\frac{\delta K}{\delta_+ \rho(\underline{r})} = \frac{\delta K[\rho_M]}{\delta \rho(\underline{r})}\Bigg|_{\rho = \rho_{N+1}} \quad , \tag{2.12a}$$

$$\frac{\delta K}{\delta_- \rho(\underline{r})} = \frac{\delta K[\rho_M]}{\delta \rho(\underline{r})}\Bigg|_{\rho = \rho_{N-1}} \quad . \tag{2.12b}$$

Eq. (2.11) demonstrates our assertion that the functional derivative of the kinetic energy is discontinuous when the density varies from the N- to the (N+1)-electron density. In this special model case, the magnitude of the discontinuity precisely equals the gap energy. In a gap-free situation, for instance the case of a metal, the above discontinuity would not have shown up. In the next section we shall discuss the more realistic case of a semiconducting system with electron-electron interactions.

3. *Interacting system*

First of all we shall have to define the notion of band gap in a semiconductor when electron-electron interactions are taken into account. The band gap will be expressed in terms of total energies of many-electron ground states with different number of electrons, in the following way: We define the lowest one-electron conduction-band energy by

$$E_c = E_{N+1} - E_N \,. \tag{3.1}$$

Here E_M is the total energy of the M-electron ground state, while the N-electron state corresponds, as before, to the charge-neutral insulating ground-state corresponding to empty one-electron conduction-bands and completely filled one-electron valence-bands. Similarly, the highest one-electron valence-band energy is defined by

$$E_v = E_N - E_{N-1} \,. \tag{3.2}$$

The gap energy is then given by the difference of E_c and E_v, that is by

$$E_g = E_c - E_v \tag{3.3a}$$

$$= E_{N+1} - 2E_N + E_{N-1} \,. \tag{3.3b}$$

In the formalism of Kohn and Sham[9] the density distribution of electrons in an M-electron ground state is determined by the normalized one-electron wave functions of a Schrödinger-type of equation

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + v_{eff}(\underline{r};M) \right] \psi_j(\underline{r};M) = \varepsilon_j(M) \psi_j(\underline{r};M) \,,$$

$$j = 1,2,3,\ldots, \quad \varepsilon_{j+1}(M) \geq \varepsilon_j(M) \,, \tag{3.4}$$

in which $v_{eff}(\underline{r},M)$ represents the self-consistent KS-effective potential for M electrons†). The exact M-electron ground-state density $\rho_M(\underline{r})$ can then be written as

$$\rho_M(\underline{r}) = \sum_{j=1}^{M} |\psi_j(\underline{r};M)|^2. \tag{3.5}$$

The potential v_{eff} in (3.4) can always be expressed as a sum of three contributions,

$$v_{eff}(\underline{r};M) = u(\underline{r}) + v_H(\underline{r};M) + v_{xc}(\underline{r};M). \tag{3.6}$$

Here $u(\underline{r})$ is the external (ionic) potential††) while the second term, v_H, is the Hartree potential†††)

$$v_H(\underline{r};M) = \int d^3r'\, v(\underline{r},\underline{r}')\, \rho_M(\underline{r}'), \tag{3.7}$$

in which $\rho_M(\underline{r})$ is given by (3.5) and $v(\underline{r},\underline{r}')$ denotes the repulsive Coulomb

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†) Eq. (3.4) is sometimes referred to as Kohn-Sham equations. Similarly, the eigenenergies $\varepsilon_j(M)$ are called Kohn-Sham single-particle energies.

††) Note that $u(\underline{r})$ is an external potential due to ions with the property that N electrons are needed to make the system as a whole charge neutral. Although in what follows, we shall vary the number of electrons present in the system, the potential will *not* be changed.

†††) Also note that the Hamiltonian of the system under consideration, in second-quantization notation, reads

$$\hat{H} = \int d^3r\, \hat{\psi}^\dagger(\underline{r}) \left\{ \frac{-\hbar^2}{2m} \nabla^2 + u(\underline{r}) \right\} \hat{\psi}(\underline{r})$$

$$+ \tfrac{1}{2} \int d^3r d^3r'\, \hat{\psi}^\dagger(\underline{r}) \hat{\psi}^\dagger(\underline{r}')\, v(\underline{r},\underline{r}')\, \hat{\psi}(\underline{r}')\, \hat{\psi}(\underline{r}),$$

where $\hat{\psi}^\dagger(\underline{r})$ and $\hat{\psi}(\underline{r})$ are creation and annihilation field operators, respectively, in the Schrödinger representation (see sec.5).

interaction potential, $v(\underline{r},\underline{r}') = e^2/(4\pi\varepsilon_o|\underline{r}-\underline{r}'|)$. [†] The third term in (3.6), v_{xc}, is the so-called exchange-correlation potential which is defined as the functional derivative of an exchange-correlation energy functional of ρ to be introduced below. Equation (3.4), (3.5) together with the *given* functional dependence of v_{eff} on $\rho_M(\underline{r})$ have to be solved self-consistently.

The total-energy functional $E_u[\rho]$ can be decomposed in the following way[2,9]

$$E_u[\rho] = K[\rho] + \int d^3r\, u(\underline{r})\rho(\underline{r}) + \tfrac{1}{2}\int d^3r d^3r'\, v(\underline{r},\underline{r}')\,\rho(\underline{r})\,\rho(\underline{r}') + E_{xc}[\rho] \quad . \tag{3.8}$$

Here, $K[\rho]$ represents the kinetic energy functional of a *hypothetical non-interacting system* which has $\rho(\underline{r})$ as electron density. The second and third terms in the right-hand side of (3.8) are purely electrostatic energies and need not further be discussed. The last term, $E_{xc}[\rho]$, is by definition the exchange-correlation energy functional. In fact, (3.8) can be considered as the definition of E_{xc}.

It should be remarked that the explicit form of E_{xc} is not known, simply because this is already so for the total energy functional itself. Similar to (2.2) and (2.3), the ground-state density $\rho_M(\underline{r})$ must be a solution of the equations

$$\delta\{E_u[\rho] - \mu_M \int d^3r\, \rho(\underline{r})\} = 0, \tag{3.9a}$$

$$\int d^3r\, \rho(\underline{r}) = M, \tag{3.9b}$$

where μ_M is again a Lagrange multiplier. Similar to the case of a non-interacting system, μ_M will be an ill-defined quantity when $M = N$, but for $M \neq N$ it is well-defined. Under the conditon that $E_{xc}[\rho]$ may be differentiated, it is immediately observed from (3.9a) that

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[†] $e = -1.6\times10^{-19}$ C is the electron charge, and $\varepsilon_o = 8.854\times10^{-2}$ Fm^{-1} is the vacuum permittivity.

$$\nu_{xc}(\underline{r};M) = \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\underline{r})}\right|_{\rho = \rho_M(\underline{r})} . \tag{3.10}$$

The density $\rho_M(\underline{r})$, given by (3.5), which follows from the self-consistent solution of (3.4) with ν_{eff} given by (3.6), (3.7) and (3.10), leads to the exact total energy of the ground state, E_M, after substitution in the total energy functional, that is

$$E_M = E_u[\rho_M] . \tag{3.11}$$

We shall now show that the quantities E_c and E_v as defined in (3.1) and (3.2) can directly be related to the Kohn-Sham single-particle energies in the following way:

$$E_c = \varepsilon_{N+1}(N+1), \tag{3.12}$$

$$E_v = \varepsilon_N(N). \tag{3.13}$$

In this connection we repeat that N is the number for which a given system with a given external potential is charge neutral. Consequently, $\varepsilon_N(N)$ refers to the highest Kohn-Sham valence-band energy of the intrinsic N-electron semiconductor with completely filled valence-band and empty conduction-band, whereas $\varepsilon_{N+1}(N+1)$ refers to the highest occupied Kohn-Sham single-electron state of the *same* semiconductor with one electron added.

In order to prove (3.12) and (3.13), we introduce a new "density function" $\rho_M(\underline{r};N)$ defined as

$$\rho_M(\underline{r};N) = \sum_{j=1}^{M} |\psi_j(\underline{r};N)|^2, \tag{3.14}$$

where the ψ_j's are the normalized solutions of (3.4) with M = N. We shall sometimes use for $\rho_M(\underline{r};N)$ the abbreviation $\rho_M(N)$.
Note that $\rho_N(\underline{r}) \equiv \rho_N(\underline{r};N)$. According to (3.2) and (3.11) we have

$$E_v = E_u[\rho_N(N)] - E_u[\rho_{N-1}(N-1)] . \tag{3.15}$$

Expanding $E_u[\rho]$ in a Taylor series around $\rho = \rho_{N-1}(N)$, we obtain[†] (see Appendix A)

[†] Note that E_u is "differentiable" in $\rho = \rho_{N-1}(N)$.

$$E_u[\rho_{N-1}(N-1)] - E_u[\rho_{N-1}(N)]$$

$$= \frac{1}{1!} \int d^3r \left. \frac{\delta E_u[\rho]}{\delta \rho(\underline{r})} \right|_{\rho = \rho_{N-1}(N)} \{\rho_{N-1}(\underline{r};N-1) - \rho_{N-1}(\underline{r};N)\}$$

$$+ \frac{1}{2!} \int d^3r d^3r' \left. \frac{\delta^2 E_u[\rho]}{\delta \rho(\underline{r}) \delta \rho(\underline{r}')} \right|_{\rho = \rho_{N-1}(N)} \{\rho_{N-1}(\underline{r};N-1) - \rho_{N-1}(\underline{r};N)\}$$

$$\times \{\rho_{N-1}(\underline{r}';N-1) - \rho_{N-1}(\underline{r}';N)\} + \ldots . \qquad (3.16)$$

However, from (3.9) it follows that [cf. (2.4)]

$$\left. \frac{\delta E_u[\rho]}{\delta \rho(\underline{r})} \right|_{\rho = \rho_{N-1}(N-1)} = \mu_{N-1}. \qquad (3.17)$$

We now *assume* that $\rho_{N-1}(\underline{r};N-1)$ and $\rho_{N-1}(\underline{r};N)$ are functions which are locally different by an infinitesimally small amount only (Koopmans' assumption[10]). Furthermore we *assume* that μ_{N-1} defined by (3.9) for a system with N-1 electrons, is infinitesimally close to $\varepsilon_N(N)$ and may be put equal to it. Thus, neglecting the effect of density fluctuations $\rho_{N-1}(\underline{r};N-1) - \rho_{N-1}(\underline{r};N)$, we may write (3.17) also as

$$\left. \frac{\delta E_u[\rho]}{\delta \rho(\underline{r})} \right|_{\rho = \rho_{N-1}(N)} = \varepsilon_N(N). \qquad (3.18)$$

Use of (3.18) in the first term of the right-hand side of (3.16) makes this term zero, since $\int d^3r\{\rho_{N-1}(\underline{r};N-1) - \rho_{N-1}(\underline{r};N)\} = 0$. The second term in (3.16) is of second order in the density fluctuations $\rho_{N-1}(\underline{r};N-1) - \rho_{N-1}(\underline{r};N)$, which we assume to be negligible. Then (3.16) allows us to write (3.15) as

$$E_v = E_u[\rho_N(N)] - E_u[\rho_{N-1}(N)] \,. \tag{3.19}$$

This result can also be expressed in a Taylor-series expansion around the density distribution $\rho = \rho_{N-1}(N)$ as

$$E_v = \frac{1}{1!} \int d^3r \left.\frac{\delta E_u[\rho]}{\delta\rho(\underline{r})}\right|_{\rho=\rho_{N-1}(N)} \{\rho_N(\underline{r};N) - \rho_{N-1}(\underline{r};N)\}$$

$$+ \frac{1}{2!} \int d^3r d^3r' \left.\frac{\delta^2 E_u[\rho]}{\delta\rho(\underline{r})\delta\rho(\underline{r}')}\right|_{\rho=\rho_{N-1}(N)} \{\rho_N(\underline{r};N) - \rho_{N-1}(\underline{r};N)\}$$

$$\times \{\rho_N(\underline{r}';N) - \rho_{N-1}(\underline{r}';N)\} + \ldots \,. \tag{3.20}$$

Because of (3.18) and [see (3.14)]

$$\rho_N(\underline{r};N) - \rho_{N-1}(\underline{r};N) = |\psi_N(\underline{r};N)|^2 \,, \tag{3.21}$$

the $\underline{r}$-integration in the first term on the right-hand side of (3.20) yields $\varepsilon_N(N)$, so that, after neglecting the second and higher order terms we obtain $E_v = \varepsilon_N(N)$, which is the desired result (3.13).

Departing from (3.1) and (3.11), the correctness of (3.12) can analogously be shown.

Thus, the gap energy E_g is related to the eigen-energies of (3.4) by [see (3.3a), (3.12) and (3.13)]

$$E_g = \varepsilon_{N+1}(N+1) - \varepsilon_N(N) \,. \tag{3.22}$$

The "energy gap" which is obtained directly from solving KS-equation (3.4) with $M = N$ and which will be denoted by E_g^{KS} is given by

$$E_g^{KS} = \varepsilon_{N+1}(N) - \varepsilon_N(N) \,. \tag{3.23}$$

The expression (3.23) for E_g^{KS} is clearly different from the expression (3.22) for the *true* gap. From numerical calculations within the LDF formalism it is well known that E_g^{KS} underestimates E_g by a substantial amount[4-8], which we will denote by Δ_g. Hence, we can write

$$E_g = E_g^{KS} + \Delta_g, \tag{3.24}$$

where, with the help of (3.22) and (3.23), Δ_g can be expressed as

$$\Delta_g = \varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N). \tag{3.25}$$

Equation (3.25) is a simple expression for the missing part of the true band-gap but, unfortunately, it is a rather formal expression, as far as the first term, $\varepsilon_{N+1}(N+1)$, concerns. The second term, $\varepsilon_{N+1}(N)$, can usually be obtained as a by-product in LDF calculations of the N-particle ground state. The next section will be entirely devoted to the derivation of an expression which is more accessible for numerical evaluation than $\varepsilon_{N+1}(N+1)$ is. It will be shown that the apparent impossibility of calculating $\varepsilon_{N+1}(N+1)$ directly, is closely related to the fact that the exchange-correlation energy functional in the HKS theory suffers from a discontinuous functional derivative similar to the one shown up by the kinetic energy functional (see sec. 2).

4. Derivation of an expression for Δ_g.

In this section we shall derive an expression for Δ_g in terms of functional derivatives of E_{xc}[11]. According to (3.1), (3.11) and (3.12) we may write

$$\varepsilon_{N+1}(N+1) = E_u[\rho_{N+1}(N+1)] - E_u[\rho_N(N)] \; . \tag{4.1}$$

Along the same lines as in the procedure around (3.15)-(3.19), it can be shown that $E_u[\rho_{N+1}(N+1)]$ can be put equal to $E_u[\rho_{N+1}(N)]$, so that we can write for (4.1)

$$\varepsilon_{N+1}(N+1) = E_u[\rho_{N+1}(N)] - E_u[\rho_N(N)] \; . \tag{4.2}$$

Using (3.8) for the two different densities $\rho_{N+1}(N)$ and $\rho_N(N)$, (4.2) can be written as

$$\begin{aligned}
\varepsilon_{N+1}(N+1) = \{ & K[\rho_{N+1}(N)] + \int d^3r \; u(\underline{r}) \; \rho_{N+1}(\underline{r};N) \\
& + \tfrac{1}{2} \int d^3r d^3r' \; v(\underline{r},\underline{r}') \; \rho_{N+1}(\underline{r};N) \rho_{N+1}(\underline{r}';N) \\
& + E_{xc}[\rho_{N+1}(N)]\} \\
& - \{K[\rho_N(N)] + \int d^3r \; u(\underline{r}) \; \rho_N(\underline{r};N) \\
& + \tfrac{1}{2} \int d^3r d^3r' \; v(\underline{r},\underline{r}') \; \rho_N(\underline{r};N) \; \rho_N(\underline{r}';N) \\
& + E_{xc}[\rho_N(N)]\} \; .
\end{aligned} \tag{4.3}$$

Since the kinetic energy functional is equal to

$$K[\rho_M(N)] = \sum_{j=1}^{M} \int d^3r\, \psi_j^*(\underline{r};N)\, \left(\frac{-\hbar^2}{2m}\nabla^2\right)\psi_j(\underline{r};N)\ , \tag{4.4}$$

we immediately find

$$K[\rho_{N+1}(N)] - K[\rho_N(N)]$$

$$= \int d^3r\, \psi_{N+1}^*(\underline{r};N)\, \left(\frac{-\hbar^2}{2m}\nabla^2\right)\, \psi_{N+1}(\underline{r};N)\,. \tag{4.5}$$

Using the KS-equation (3.4) with M = N we can write

$$\left(\frac{-\hbar^2}{2m}\nabla^2\right)\, \psi_{N+1}(\underline{r};N) = \varepsilon_{N+1}(N)\, \psi_{N+1}(\underline{r};N)$$

$$- \nu_{eff}(\underline{r};N)\, \psi_{N+1}(\underline{r};N)\,, \tag{4.6}$$

where $\nu_{eff}(\underline{r};N)$ is given by [cf. (3.6)]

$$\nu_{eff}(\underline{r};N) \simeq u(\underline{r}) + \nu_H(\underline{r};N) + \nu_{xc}^{(-)}(\underline{r})\,, \tag{4.7}$$

in which we have introduced $\nu_{xc}^{(-)}$, defined by [cf. (3.10)]

$$\nu_{xc}^{(-)}(\underline{r}) = \left.\frac{\delta E_{xc}[\rho]}{\delta\, \rho(\underline{r})}\right|_{\rho\, =\, \rho_{N-1}(N-1)}$$

$$= \frac{\delta E_{xc}}{\delta \rho(\underline{r})}\ . \tag{4.8}$$

The necessity of introducing (4.8) stems from the observation that the functional derivative in $\rho = \rho_N(N)$ does not exist (compare with (2.12b) where a similar discontinuity occurred in the functional derivative of the kinetic energy). Now, (4.5) can be written as

$$K[\rho_{N+1}(N)] - K[\rho_N(N)]$$

$$= \varepsilon_{N+1}(N) - \int d^3r\, u(\underline{r})\ \delta\rho_{N+1}(\underline{r};N)$$

$$- \int d^3r d^3r'\, v(\underline{r},\underline{r}')\ \{\delta\rho_{N+1}(\underline{r};N)\}\rho_N(\underline{r}';N)$$

$$- \int d^3r\, v_{xc}^{(-)}(\underline{r})\ \delta\rho_{N+1}(\underline{r};N), \tag{4.9}$$

where $\delta\rho_{N+1}(\underline{r};N)$ denotes the density variation,

$$\delta\rho_{N+1}(\underline{r};N) = \psi^*_{N+1}(\underline{r};N)\ \psi_{N+1}(\underline{r};N). \tag{4.10}$$

After substitution of (4.9) in (4.3), we observe that the terms involving $u(\underline{r})$ cancel precisely. Furthermore we have, to the first order in $\delta\rho_{N+1}(\underline{r};N)$,

$$\frac{1}{2}\int d^3r d^3r'\, v(\underline{r},\underline{r}')\ \rho_{N+1}(\underline{r};N)\ \rho_{N+1}(\underline{r}';N)$$

$$= \frac{1}{2}\int d^3r d^3r'\, v(\underline{r},\underline{r}')\ \rho_N(\underline{r};N)\rho_N(\underline{r}';N)$$

$$+ \int d^3r d^3r'\, v(\underline{r},\underline{r}')\ \{\delta\rho_{N+1}(\underline{r};N)\}\ \rho_N(\underline{r}';N). \tag{4.11}$$

We can now write (4.3), by substitution of (4.9) and (4.11), as [see also (3.25)]

$$\varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N) = \Delta_g$$

$$= E_{xc}[\rho_{N+1}(N)] - E_{xc}[\rho_N(N)]$$

$$- \int d^3r\, \psi^*_{N+1}(\underline{r};N)\ v_{xc}^{(-)}(\underline{r})\ \psi_{N+1}(\underline{r};N). \tag{4.12}$$

The quantity $E_{xc}[\rho_{N+1}(N)] - E_{xc}[\rho_N(N)]$ can also be expressed (using a Taylor-series expansion around $\rho_{N+1}(N)$ and omitting second and higher order corrections) as[†)]

$$E_{xc}[\rho_{N+1}(N)] - E_{xc}[\rho_N(N)]$$

$$= -\int d^3r \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\underline{r})}\right|_{\rho = \rho_{N+1}(\underline{r};N)} \{\rho_N(\underline{r};N) - \rho_{N+1}(\underline{r};N)\}$$

$$= \int d^3r\, \psi^*_{N+1}(\underline{r};N)\, v^{(+)}_{xc}(\underline{r})\, \psi_{N+1}(\underline{r};N)\,. \qquad (4.13)$$

Here we have introduced $v^{(+)}_{xc}(\underline{r})$ by defining

$$v^{(+)}_{xc}(\underline{r}) = \left.\frac{\delta E_{xc}[\rho]}{\delta\rho(\underline{r})}\right|_{\rho = \rho_{N+1}(N)}$$

$$= \frac{\delta E_{xc}}{\delta_+\rho(\underline{r})}\,. \qquad (4.14)$$

Note that in writing down the Taylor expansion (4.13), we have assumed that the exchange-correlation functional is continuous itself, implying that $E_{xc}[\rho_N(N)]$ is a well-defined quantity (contrary to its derivation which does not exist at the density $\rho_N(N)$).

After substitution of the right-hand side of (4.13) in (4.12), we arrive at the desired relation

$$\Delta_g = \int d^3r\, \psi^*_{N+1}(\underline{r};N)\, \{v^{(+)}_{xc} - v^{(-)}_{xc}\}\, \psi_{N+1}(\underline{r};N)\,. \qquad (4.15)$$

However, it should be noted that this equation is a rather formal expression for Δ_g, since the density functional theory does not afford the prescription of constructing the exchange-correlation energy functional and as such (4.15) would be of no practical use. Hence, in order to take advantage of (4.15), it will be essential to derive an explicit expression for E_{xc}.

[†)] Note that, $E_{xc}[\rho]$ can not be expanded around $\rho = \rho_N(N)$, since it is not "differentiable" there.

5. *Green's function approach to the exchange-correlation energy functional*

This section is entirely devoted to the derivation of an expression for the exchange-correlation energy functional, which has been introduced in section 3 (see (3.8)]. The expression to be obtained will enable us in section 6 to rewrite the Δ_g-expression of section 4 in a form more suited for actual calculation.

In dealing with our many-electron system we shall employ a Green function method of treatment.[12-14] Within this treatment a vital role is played by the *one-particle* Green function. In the framework of this formalism, an expression for the exchange-correlation energy functional will be derived.

Let us denote the Hamiltonian of the system under consideration as follows

$$\hat{\tilde{H}} = \hat{\tilde{T}} + \hat{\tilde{U}} + \hat{\tilde{V}}, \tag{5.1}$$

where $\hat{\tilde{T}}$, $\hat{\tilde{U}}$ and $\hat{\tilde{V}}$ are the kinetic energy, the external (ionic) potential energy, and the electron-electron Coulomb interaction energy operators, respectively[†]. In second-quantization representation we have:

$$\hat{\tilde{T}} = \int d^3r\, \hat{\tilde{\psi}}^{\dagger}(\underline{r}) \left(\frac{-\hbar^2}{2m}\nabla^2\right)\hat{\tilde{\psi}}(\underline{r}), \tag{5.2}$$

$$\hat{\tilde{U}} = \int d^3r \hat{\tilde{\psi}}^{\dagger}(\underline{r})\, u(\underline{r})\, \hat{\tilde{\psi}}(\underline{r}), \tag{5.3}$$

and

$$\hat{\tilde{V}} = \tfrac{1}{2} \int d^3r d^3r'\, \hat{\tilde{\psi}}^{\dagger}(\underline{r})\, \hat{\tilde{\psi}}^{\dagger}(\underline{r'})\, v(\underline{r},\underline{r'})\, \hat{\tilde{\psi}}(\underline{r'})\, \hat{\tilde{\psi}}(\underline{r}). \tag{5.4}$$

Here, $\hat{\tilde{\psi}}^{\dagger}(\underline{r})$ and $\hat{\tilde{\psi}}(\underline{r})$ are *creation* and *annihilation* field operators, respectively, in the Schrödinger representation[††].

[†] We use carets (^) to distinguish operators from their c-number counterparts.

[††] Note that, in the Schrödinger representation the operators do not depend on time.

In order to obtain an expression for the total energy, and subsequently one for the exchange-correlation energy functional E_{xc}, we shall employ a *perturbation method*. We introduce a coupling constant λ which can assume all values from 0 up to 1, and a Hamiltonian

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{H}_1 \ . \tag{5.5}$$

Here $\hat{H}_0$ is the Kohn-Sham Hamiltonian

$$\hat{H}_0 = \hat{T} + \hat{v}_{eff} \ , \tag{5.6}$$

with

$$\hat{v}_{eff} = \int d^3r \ \hat{\psi}^\dagger(\underline{r}) v_{eff}(\underline{r}) \hat{\psi}(\underline{r}) \ , \tag{5.7}$$

while $\hat{H}_1$ is the perturbing Hamiltonian given by

$$\hat{H}_1 = \hat{V} - \hat{W} \ , \tag{5.8}$$

in which

$$\hat{W} = \hat{v}_{eff} - \hat{U} \ . \tag{5.9}$$

It is important to realize that the one-particle effective potential of Kohn and Sham, $v_{eff}(\underline{r})$, takes into account the effects of electron-electron interaction in such a manner that the obtained electron density is *exact*. To be specific, denoting the ground-state of the "Kohn-Sham system", which is just a single Slater determinant of order M,[†)] by $|\Psi_0\rangle_S$ and that of the real system, being a vector in the space spanned by all the Slater determinants of order M, by $|\Psi_1\rangle_S$, one has

$$\rho_M^{KS}(\underline{r}) = {}_S\langle \Psi_0 | \hat{\psi}^\dagger(\underline{r}) \ \hat{\psi}(\underline{r}) | \Psi_0 \rangle_S$$

$$= \rho_M(\underline{r}) = {}_S\langle \Psi_1 | \hat{\psi}^\dagger(\underline{r}) \hat{\psi}(\underline{r}) | \Psi_1 \rangle_S \ . \tag{5.10}$$

Note that the subscript S, in e.g. $|\Psi_0\rangle_S$, indicates that the corresponding

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[†)] M is the number of electrons in the system.

state vector is in the Schrödinger representation. It is immediately verified that for $\lambda = 1$ the operator in (5.5) coincides with the original Hamiltonian operator (5.1). By introducing the local potential

$$w(\underline{r}) = v_{eff}(\underline{r}) - u(\underline{r}) \ , \tag{5.11}$$

the operator $\hat{W}$ can be expressed as

$$\hat{W} = \int d^3r \ \hat{\psi}^{\dagger}(\underline{r}) w(\underline{r}) \hat{\psi}(\underline{r}) . \tag{5.12}$$

Let us denote the normalized ground state of $\hat{H}(\lambda)$ with $\lambda \in [0,1]$ by $|\Psi_\lambda\rangle_S$ [†)] and the corresponding eigen-energy by $E(\lambda)$. According to a theorem due to Feynman[15] we can write

$$\frac{\partial}{\partial\lambda} E(\lambda) = {}_S\langle\Psi_\lambda| \ (\partial\hat{H}(\lambda)/\partial\lambda) \, |\Psi_\lambda\rangle_S \ . \tag{5.13}$$

By integrating both sides of (5.13) over the interval $[0,\lambda]$, we can immediately write

$$E(\lambda) = E(0) + \int_0^\lambda \frac{d\lambda'}{\lambda'} \, {}_S\langle\Psi_{\lambda'}|\lambda'\hat{H}_1|\Psi_{\lambda'}\rangle_S , \tag{5.14}$$

where

$$E(0) = {}_S\langle\Psi_0|\hat{H}_0|\Psi_0\rangle_S \ . \tag{5.15}$$

If $\{\psi_j(\underline{r};M)\}$ denotes the *complete* orthonormal set of Kohn-Sham one-electron wave functions, then we can write

$$\hat{\psi}^{\dagger}(\underline{r}) = \sum_j \psi_j^*(\underline{r};M)\hat{c}_j^{\dagger}(M) , \tag{5.16a}$$

$$\hat{\psi}(\underline{r}) = \sum_j \psi_j(\underline{r};M) \, \hat{c}_j(M) . \tag{5.16b}$$

Here $\hat{c}_j^{\dagger}(M)$ and $\hat{c}_j(M)$ are the creation and annihilation operators of the

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[†)] Note that our older definitions of $|\Psi_0\rangle_S$ and $|\Psi_1\rangle_S$ are consistent with this general definition.

jth one-electron state of the M-electron "Kohn-Sham system", respectively. They satisfy the anti-commutation relations

$$[\hat{c}_j^\dagger(M),\ \hat{c}_k^\dagger(M)]_+ = [\hat{c}_j(M),\ \hat{c}_k(M)]_+ = 0, \tag{5.17a}$$

$$[\hat{c}_j^\dagger(M),\ \hat{c}_k(M)]_+ = \delta_{j,k}, \tag{5.17b}$$

where $\delta_{j,k}$ stands for the Kronecker δ-function. It is then easily verified for the M-particle ground state that[†] [See (3.14) and (4.4)]

$$\begin{aligned} E(0) &= \sum_{j=1}^{M} \int d^3r \psi_j^*(\underline{r};M)\ \left(\frac{-\hbar^2}{2m}\nabla^2\right)\psi_j(\underline{r};M) \\ &\quad + \int d^3r\ v_{eff}(\underline{r}) \sum_{j=1}^{M} |\psi_j(\underline{r};M)|^2 \\ &= K[\rho_M(M)] + \int d^3r\ v_{eff}(\underline{r})\rho_M(\underline{r};M). \end{aligned} \tag{5.18}$$

This relation will be used in a later discussion.

We shall now try to obtain an expression for the expectation value ${}_S\langle\Psi_\lambda|\lambda\hat{H}_1|\Psi_\lambda\rangle_S$ in terms of a *one-particle* Green function and the related *mass operator*, both to bo defined below, such that the λ'-integration in (5.14) can be performed. To this end, let $\Lambda_\lambda(t,t') = \exp[-i\,\hat{H}(\lambda)(t-t')/\hbar]$ be the time-evolution operator connecting the state vector $|\Psi_\lambda(t')\rangle_S$ with $|\Psi_\lambda(t)\rangle_S$,

$$|\Psi_\lambda(t)\rangle_S = \Lambda_\lambda(t,t')|\Psi_\lambda(t')\rangle_S, \tag{5.19}$$

in the Schrödinger representation. We then have for the *field operators* in the Heisenberg representation

$$\hat{\psi}_\lambda^\dagger(\underline{r}t) = \Lambda_\lambda(0,t)\hat{\psi}^\dagger(\underline{r})\ \Lambda_\lambda(t,0), \tag{5.20a}$$

$$\hat{\psi}_\lambda(\underline{r}t) = \Lambda_\lambda(0,t)\ \hat{\psi}(\underline{r})\ \Lambda_\lambda(t,0). \tag{5.20b}$$

[†] Note that the argument M in $v_{eff}(\underline{r};M)$ has been suppressed here.

The equation of motion for the annihilation field operator $\hat{\psi}_\lambda(\underline{r}t)$ reads[†1]

$$i\hbar\,(\partial\hat{\psi}_\lambda(\underline{r}t)/\partial t)$$

$$= [\hat{\psi}_\lambda(\underline{r}t)\,,\ \hat{H}_{0\lambda}(t)\,]_- + [\hat{\psi}_\lambda(\underline{r}t)\,,\ \lambda\hat{H}_{1\lambda}(t)\,]_- \,. \tag{5.21}$$

Here $\hat{H}_{0\lambda}(t)$ and $\hat{H}_{1\lambda}(t)$ are Heisenberg representations of $\hat{H}_0$ and $\hat{H}_1$, respectively. It should be noted, however, that since $\hat{H}(\lambda)$ commutes with $\Lambda_\lambda(t,t')$ one could have also maintained the operators $\hat{H}_0$ and $\hat{H}_1$ themselves in the right-hand side of (5.21). By making use of (5.16), (5.17), (5.20) and the completeness relation of the one-particle wave functions $\psi_j(\underline{r};M)$, $\sum_j \psi_j(\underline{r};M)\psi_j^*(\underline{r}';M) = \delta(\underline{r},\underline{r}')$, one can readily arrive at the *equal-time* anti-commutation relations of the field operators

$$[\hat{\psi}_\lambda^\dagger(\underline{r}t)\,,\hat{\psi}_\lambda^\dagger(\underline{r}'t)\,]_+ = [\hat{\psi}_\lambda(\underline{r}t)\,,\hat{\psi}_\lambda(\underline{r}'t)\,]_+ = 0\ , \tag{5.22a}$$

$$[\hat{\psi}_\lambda^\dagger(\underline{r}t)\,,\hat{\psi}_\lambda(\underline{r}'t)\,]_+ = \delta(\underline{r}-\underline{r}')\ . \tag{5.22b}$$

Using (5.22) it is straightforward to obtain

$$[\hat{\psi}_\lambda(\underline{r}t)\,,\hat{H}_{0\lambda}(t)\,]_- = -\left\{\frac{\hbar^2}{2m}\nabla^2 - v_{\text{eff}}(\underline{r})\right\}\hat{\psi}_\lambda(\underline{r}t)\ . \tag{5.23}$$

Hence, (5.21) can be written as

$$\left\{i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 - v_{\text{eff}}(\underline{r})\right\}\hat{\psi}_\lambda(\underline{r}t) = [\hat{\psi}_\lambda(\underline{r}t)\,,\ \lambda\hat{H}_1(t)\,]_-\,. \tag{5.24}$$

Let us multiply (5.24) on the right with $\hat{\psi}_\lambda^\dagger(\underline{r}'t')$ and apply Wick's time-ordering operator T_w, defined for fermion operators by

$$T_w\{\hat{A}_1(t_1)\hat{A}_2(t_2)\ldots\hat{A}_n(t_n)\} = \sum_P (-1)^P\,\hat{A}_{P1}(t_{P1})\hat{A}_{P2}(t_{P2})$$

$$\times\ldots\hat{A}_{Pn}(t_{Pn})\Theta(t_{P1}-t_{P2})\Theta(t_{P2}-t_{P3})\ldots\Theta(t_{P(n-1)}-t_{Pn})\ , \tag{5.25}$$

[†1] We use in our text $[,]_-$ for commutation and $[\ ,\ ]_+$ for anti-commutation.

to the resulting equation ($\hat{A}_j(t_j)$ is either $\hat{\psi}^\dagger_\lambda(\underline{r}t)$ or $\hat{\psi}_\lambda(\underline{r}t)$; P is a permutation of 1,2,...,n, with parity p; and $\Theta(t)$ is the unit step-function). Let us subsequently take the expectation value of both sides in the Heisenberg ground state $|\Psi_\lambda\rangle_H$. The result can be written as

$$\left[i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 - v_{eff}(\underline{r})\right] G_{1\lambda}(\underline{r}t,\underline{r}'t')$$

$$= \hbar\,\delta(t-t')\delta(\underline{r}-\underline{r}')$$

$$- i\,{}_H\langle\Psi_\lambda|\,T_w\{[\hat{\psi}_\lambda(\underline{r}t),\,\lambda\hat{H}_{1\lambda}(t)]_-\,\hat{\psi}^\dagger_\lambda(\underline{r}'t')\}|\Psi_\lambda\rangle_H. \tag{5.26}$$

Here, we have introduced the one-particle Green function $G_{1\lambda}$, defined as

$$G_{1\lambda}(1,2) \overset{\Delta}{=} -i\,{}_H\langle\Psi_\lambda|T_w\{\hat{\psi}_\lambda(1)\hat{\psi}^\dagger_\lambda(2)\}|\Psi_\lambda\rangle_H\,, \tag{5.27}$$

where the arguments j = 1,2, stand for the space-time four-vector $(\underline{r}_j,t_j)$. In deriving (5.26) use has been made of $\partial\Theta(t)/\partial t = \delta(t)$, and of the anti-commutation relation (5.22b). One immediate consequence of (5.26) is that G_{10} satisfies the equation of motion

$$\left[i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla_1^2 - v_{eff}(\underline{r}_1)\right] G_{10}(1,2) = \hbar\delta(1,2)\,, \tag{5.28}$$

where $\delta(1,2)$ represents the four-dimensional Dirac δ-function, $\delta(1,2) = \delta(t_1-t_2)\delta(\underline{r}_1-\underline{r}_2)$.

By introducing, quite generally, the so-called *"mass operator"* $M_\lambda(1,2)$ through the relation

$${}_H\langle\Psi_\lambda|T_w\{[\hat{\psi}_\lambda(1),\,\lambda\hat{H}_{1\lambda}(t_1)]_-\hat{\psi}^\dagger_\lambda(2)\}|\Psi_\lambda\rangle_H$$

$$= i\hbar\int d(3)\,M_\lambda(1,3)\,G_{1\lambda}(3,2), \tag{5.29}$$

it is easily shown (by substitution in (5.26)) that the Green functions $G_{1\lambda}$ and G_{10} are interrelated by means of

$$G_{1\lambda}(1,2) = G_{10}(1,2) + \int d(3)d(4)G_{10}(1,3)M_\lambda(3,4)G_{1\lambda}(4,2)\,, \tag{5.30a}$$

(Dyson's equation) or, symbolically,

$$G_{1\lambda} = G_{10} + G_{10} M_\lambda G_{1\lambda}. \tag{5.30b}$$

It has become common practice to represent (5.30b) and related expressions in diagramatic form. In Appendix B the main features of the diagrammatic approach, in so far as is necessary to achieve our goals, are recapitulated.

In order to lay the connection with the expectation value in the right-hand side of (5.14) it is useful to consider in (5.29) the limiting situation in which $\underline{r}_2 \to \underline{r}_1$ and $t_2 \downarrow t_1$ (from the upper side i.e. $t_2 = t_1 + \eta$ with $\eta > 0$ while $\eta \to 0$). By convenient combination of (5.26), (5.28), (5.29) and, after that, integration over $\underline{r}_1$, we can derive the relation

$$-i\int d^3r_1 \lim_{\substack{t_2\downarrow t_1 \\ \underline{r}_2\to\underline{r}_1}} [i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla_1^2 - v_{eff}(\underline{r}_1)]\{G_{1\lambda}(1,2) - G_{10}(1,2)\}$$

$$= \int d^3r_1 \lim_{\underline{r}_2\to\underline{r}_1} {}_H\langle\Psi_\lambda|\tilde{\psi}_\lambda^\dagger(\underline{r}_2 t_1)[\tilde{\psi}_\lambda(\underline{r}_1 t_1), \lambda\tilde{H}_{1\lambda}(t_1)]_- |\Psi_\lambda\rangle_H$$

$$= -i\hbar\int d^3r_1 \lim_{\substack{t_1\downarrow t_1 \\ \underline{r}_2\to\underline{r}_1}} \int d(3)\, M_\lambda(1,3)\, G_{1\lambda}(3,2) = -i\hbar \mathrm{Tr}\{M_\lambda G_{1\lambda}\}. \tag{5.31}$$

In the last step we have introduced the trace operation, defined by †)

$$\mathrm{Tr}\{A_1 A_2 \ldots A_N\} = \int d^3r_1 \lim_{\substack{t_{N+1}\downarrow t_1 \\ \underline{r}_{N+1}\to\underline{r}_N}} \int d(2) \ldots \int d(N)$$

$$\times A_1(\underline{r}_1 t_1, \underline{r}_2 t_2) A_2(\underline{r}_2 t_2, \underline{r}_3 t_3) \ldots A_N(\underline{r}_N t_N, \underline{r}_{N+1} t_{N+1}), \tag{5.32}$$

where A_j represents any two-point function.

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†) It can be easily proven that this trace operation has the cyclical property $\mathrm{Tr}\{A_1 A_2 \ldots A_N\} = \mathrm{Tr}\{A_N A_1 \ldots A_{N-1}\}$, etc., provided that the functions $A_j(\underline{r}t, \underline{r}'t')$ with respect to their time dependence, are functions of $t-t'$ only.

By employing (5.22) and some algebra one easily arrives at [See (5.8), (5.9) and (5.11)]

$$[\,\hat{\psi}_\lambda(\underline{r}_1 t_1),\ \lambda\hat{H}_{1\lambda}(t_1)\,]_- = 2\lambda\Big\{\frac{1}{2}\,[\int d^3r'\ \hat{\psi}^\dagger_\lambda(\underline{r}' t_1)$$

$$\times\, v(\underline{r}_1,\underline{r}')\ \hat{\psi}_\lambda(\underline{r}' t_1)\,] - w(\underline{r}_1)\Big\}\,\hat{\psi}_\lambda(\underline{r}_1 t_1) + \lambda w(\underline{r}_1)\ \hat{\psi}_\lambda(\underline{r}_1 t_1)\,. \tag{5.33}$$

Hence, for the right-hand side of (5.31) we can write

$$\int d^3r_1 \lim_{\underline{r}_2 \to \underline{r}_1} {}_H\langle\Psi_\lambda|\hat{\psi}^\dagger_\lambda(\underline{r}_2 t_1)[\hat{\psi}_\lambda(\underline{r}_1 t_1),\ \lambda\hat{H}_{1\lambda}(t_1)]_-|\Psi_\lambda\rangle_H$$

$$= 2\,{}_H\langle\Psi_\lambda|\Lambda_\lambda(0,t_1)\ \lambda\Big\{\frac{1}{2}\int d^3r d^3r'\ \hat{\psi}^\dagger(\underline{r})\ \hat{\psi}^\dagger(\underline{r}')$$

$$\times v(\underline{r},\underline{r}')\ \hat{\psi}(\underline{r}')\ \hat{\psi}(\underline{r}) - \int d^3r\ \hat{\psi}^\dagger(\underline{r}) w(\underline{r})\ \hat{\psi}(\underline{r})\Big\}$$

$$\times\Lambda_\lambda(t_1,0)\,|\,\Psi_\lambda\rangle_H$$

$$+\ \lambda\,{}_H\langle\Psi_\lambda|\int d^3r\ \hat{\psi}^\dagger(\underline{r}t_1)\ w(\underline{r})\ \hat{\psi}(\underline{r}t_1)\,|\Psi_\lambda\rangle_H$$

$$= 2\ {}_S\langle\Psi_\lambda|\lambda\hat{H}_1|\Psi_\lambda\rangle_S + \lambda\,{}_H\langle\Psi_\lambda|\hat{\bar{w}}(t_1)\,|\Psi_\lambda\rangle_H\ . \tag{5.34}$$

Here use has been made of the transformation relation

$$|\Psi_\lambda(t)\rangle_S = \Lambda_\lambda(t,0)\,|\Psi_\lambda\rangle_H\ . \tag{5.35}$$

The first term in the right-hand side of (5.34) is proportional to the integrand in (5.14), while the second term can be written

$$\lambda\,{}_H\langle\Psi_\lambda|\ \hat{\bar{w}}(t_1)\,|\,\Psi_\lambda\rangle_H = \lambda\int d^3r_1 w(\underline{r}_1)$$

$$\times\ {}_H\langle\Psi_\lambda|\hat{\psi}^\dagger_\lambda(\underline{r}_1 t_1)\ \hat{\psi}_\lambda(\underline{r}_1 t_1)\,|\ \Psi_\lambda\rangle_H$$

$$= -i\lambda \int d^3 r_1 \lim_{\substack{t_2 \downarrow t_1 \\ \underline{r}_2 \to \underline{r}_1}} \int d(3)\ \omega(1,3) G_{1\lambda}(3,2)$$

$$= -i\lambda\ \mathrm{Tr}\{\omega G_{1\lambda}\} . \tag{5.36}$$

Here use has been made of (5.27), while the two-point function ω is defined as

$$\omega(1,2) = w(\underline{r}_1)\ \delta(1,2) . \tag{5.37}$$

It now follows from (5.31), (5.34) and (5.36) that

$${}_S\langle \Psi_\lambda | \lambda\ \hat{H}_1 | \Psi_\lambda \rangle_S = \frac{1}{2i}\ \mathrm{Tr}\{[\hbar M_\lambda - \lambda\omega]\ G_{1\lambda}\} , \tag{5.38}$$

and this can be substituted in (5.14) to yield

$$E(\lambda) = E(0) + \int_0^\lambda \frac{d\lambda'}{2i\lambda'}\ \mathrm{Tr}\{[\hbar M_{\lambda'} - \lambda'\omega]\ G_{1\lambda'}\} . \tag{5.39}$$

In Appendix B it is outlined that the mass operator M_λ may be expanded in a series, each term of which can be represented by a Feynman diagram. There we have pointed out that for the calculation of the mass operator, one may consider the so-called *skeleton* M- diagrams only, in which the full lines represent Green functions $G_{1\lambda}$. Each term of the series (or the contribution of each skelton M- diagramm) is proportional to an integral over all internal space-time variables (See Appendix B) of a product of Green functions and interaction functions. Calling the number of interaction functions in each term (or diagram) the *order* of it, one can easily show that, to an nth-order M_λ-term (2n-1) Green functions contribute. The only exception to this rule is the *first order* term (n=1) involving a w-interaction, in which case no Green function contributes. As each interaction function in a term carries a factor λ, it is obvious that an nth-order term is proportional to λ^n. Hence, the *explicit* dependence of an nth-order term on λ, is λ^n. However, since the Green functions $G_{1\lambda}$ themselves also depend on λ, there is an additional *implicit* λ-dependence. Let $M_\lambda^{(n)}$ represent the contribution of *all* nth-order mass operator terms (or skeleton M-diagrams), and let $\bar{M}_\lambda^{(n)}$ be defined by [16]

$$\bar{M}_\lambda^{(n)} = \lambda^{-n} M_\lambda^{(n)} \quad . \tag{5.40}$$

Thus, the λ-dependence of $\bar{M}_\lambda^{(n)}$ is completely implicit and we can write

$$M_\lambda = \sum_{n=1}^{\infty} M_\lambda^{(n)}$$

$$= \sum_{n=1}^{\infty} \lambda^n \bar{M}_\lambda^{(n)} . \tag{5.41}$$

By substitution of (5.41) in the right-hand side of (5.39) we find

$$E(\lambda) - E(0) = \frac{1}{2i} \sum_{n=1}^{\infty} \int_0^\lambda \frac{d\lambda'}{\lambda'} \lambda'^n \mathrm{Tr}\{\hbar \bar{M}_{\lambda'}^{(n)} G_{1\lambda'}\}$$

$$- \frac{1}{2i} \mathrm{Tr}\{\omega \int_0^\lambda d\lambda' G_{1\lambda'}\} . \tag{5.42}$$

We integrate the first term in the right-hand side of (5.42) by parts, with the result

$$\frac{1}{2i} \sum_{n=1}^{\infty} \int_0^\lambda \frac{d\lambda'}{\lambda'} \lambda'^n \mathrm{Tr}\{\hbar \bar{M}_{\lambda'}^{(n)} G_{1\lambda'}\}$$

$$= - i \sum_{n=1}^{\infty} \frac{\lambda^n}{2n} \mathrm{Tr}\{\hbar \bar{M}_\lambda^{(n)} G_{1\lambda}\}$$

$$+ i \sum_{n=1}^{\infty} \frac{1}{2n} \int_0^\lambda d\lambda' \lambda'^n \frac{\partial}{\partial \lambda'} \mathrm{Tr}\{\hbar \bar{M}_{\lambda'}^{(n)} G_{1\lambda'}\} . \tag{5.43}$$

From the fact that each term contributing to $\bar{M}_{\lambda'}^{(n)}$ contains a product of (2n-1) functions $G_{1\lambda'}$ (recall the one exception, mentioned earlier!), and owing to the cyclical property of Tr,[†] we easily derive for n = 1,2,...,

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[†] Note that all two point functions which we deal with (e.g. $G_{1\lambda}$ and M_λ), depend on the difference of their time arguments only, which is a consequence of the fact that the Hamiltonian of our system is independent of time.

$$\frac{\partial}{\partial\lambda'}\,\mathrm{Tr}\{\hbar\bar{M}^{(n)}_{\lambda'}G_{1\lambda'}\} = 2n\mathrm{Tr}\{\hbar\bar{M}^{(n)}_{\lambda'}\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}$$

$$+\,\mathrm{Tr}\{\omega\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}\,\delta_{n,1}. \tag{5.44}$$

Note that the last term in the right-hand side of (5.44) has indeed to be added in order to compensate for half of $2\frac{\partial}{\partial\lambda'}\,\mathrm{Tr}\{\hbar\frac{-i}{\hbar}\omega\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}$ in the first term. Substituion of (5.44) in the second term in the right-hand side of (5.43) yields

$$i\sum_{n=1}^{\infty}\frac{1}{2n}\int_0^{\lambda}d\lambda'\,\lambda'^{n}\frac{\partial}{\partial\lambda'}\,\mathrm{Tr}\{\hbar\bar{M}^{(n)}_{\lambda'}\,G_{1\lambda'}\}$$

$$= i\hbar\,\mathrm{Tr}\{\int_0^{\lambda}d\lambda' M_{\lambda'}\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}$$

$$+\frac{i}{2}\,\mathrm{Tr}\{\omega\int_0^{\lambda}d\lambda'\lambda'\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}. \tag{5.45}$$

Integrating the last term in (5.45) by parts gives

$$\frac{i}{2}\,\mathrm{Tr}\{\omega\int_0^{\lambda}d\lambda'\lambda'\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}$$

$$= \frac{i}{2}\,\mathrm{Tr}\{\lambda\omega G_{1\lambda}\} - \frac{i}{2}\,\mathrm{Tr}\{\omega\int_0^{\lambda}d\lambda'\,G_{1\lambda'}\}. \tag{5.46}$$

We can now combine (5.43), (5.45), and (5.46), and substitute the result in (5.42), which brings us to the result

$$E(\lambda) - E(0) = i\hbar\,\mathrm{Tr}\{\int_0^{\lambda}d\lambda' M_{\lambda'}\frac{\partial G_{1\lambda'}}{\partial\lambda'}\}$$

$$-i\Big\{\frac{1}{2}\,\mathrm{Tr}\{[\hbar M^{(1)}_{\lambda} - \lambda\omega]G_{1\lambda}\}$$

$$+\sum_{n=2}^{\infty}\frac{1}{2n}\,\mathrm{Tr}\{\hbar M^{(n)}_{\lambda}G_{1\lambda}\}\Big\}. \tag{5.47}$$

This can be written more compactly by introducing the function $Y(\lambda)$ defined as

$$Y(\lambda) = \sum_{n=1}^{\infty} Y^{(n)}(\lambda) \ , \tag{5.48}$$

where

$$Y^{(1)}(\lambda) = \frac{1}{2} \mathrm{Tr}\{[\hbar M_{\lambda}^{(1)} - \lambda\omega] \, G_{1\lambda}\}, \tag{5.49a}$$

$$Y^{(n)}(\lambda) = \frac{1}{2n} \mathrm{Tr}\{\hbar M_{\lambda}^{(n)} G_{1\lambda}\}, \text{ for } n > 1. \tag{5.49b}$$

In terms of $Y(\lambda)$ (5.47) reads

$$E(\lambda) = E(0) + i\hbar \, \mathrm{Tr} \, \{\int_0^{\lambda} d\lambda' M_{\lambda'} \frac{\partial G_{1\lambda'}}{\partial \lambda'}\} - i \, Y(\lambda) \ , \tag{5.50}$$

which is almost the desired result.

The last step in arriving at the final result for $E(\lambda)$ is to rewrite the second term in the right-hand side of (5.50). This is achieved by starting with Dyson's equation which may alternatively be written as[†)]

$$G_{1\lambda} = G_{10} + G_{1\lambda} M_{\lambda} G_{10}, \tag{5.51}$$

or,

$$G_{1\lambda} = G_{10}(1 - M_{\lambda} G_{10})^{-1}. \tag{5.52}$$

Hence, the second term in the right-hand side of (5.50) can be written as

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†) Incidentally we note that the Dyson equation (5.51), usually called the *adjoint* or "*time-reversed*" version of (5.30), is completely equivalent with (5.30). Equation (5.51) can be obtained directly, for instance, if one, instead of departing from the equation of motion for the annihilation field operator $\tilde{\psi}_{\lambda}(\underline{r}t)$, as in (5.21), starts with the equation of motion of the creation field operator $\tilde{\psi}_{\lambda}^{\dagger}(\underline{r}t)$.

$$i\hbar\, \mathrm{Tr}\{ \int_0^\lambda d\lambda'\, M_{\lambda'} \frac{\partial G_{1\lambda'}}{\partial \lambda'} \}$$

$$= i\hbar\, \mathrm{Tr}\{ \int_0^\lambda M_{\lambda'} G_{10}\, d(1 - M_{\lambda'} G_{10})^{-1} \}$$

$$= i\hbar\, \mathrm{Tr}\{ M_\lambda G_{10}\, (1 - M_\lambda G_{10})^{-1} \}$$

$$- i\hbar\, \mathrm{Tr}\{ \int_0^\lambda (1 - M_{\lambda'} G_{10})^{-1}\, d(M_{\lambda'} G_{10}) \}$$

$$= i\hbar\, \mathrm{Tr}\{ M_\lambda G_{1\lambda} + \ln(1 - M_\lambda G_{10}) \} . \qquad (5.53)$$

Here use has been made of the fact $M_\lambda\big|_{\lambda = 0} = 0$, (see (5.29)). In view of (5.53), eq. (5.50) can be written as

$$E(\lambda) = E(0) + i\hbar\, \mathrm{Tr}\{ \ln(1 - M_\lambda G_{10}) + M_\lambda G_{1\lambda} \} - i\, Y(\lambda) , \qquad (5.54)$$

which is the desired result for $E(\lambda)$.

Our next task is to obtain from (5.54) an expression for the exchange-correlation energy functional. The latter is defined by (3.8). According to the HK-theorem, $E_u[\rho]$ is equal to the exact total energy of the system if ρ is equal to the exact density. By taking the functions participating in (5.54) as functionals of the electron density ρ, we may equate the right-hand sides of (3.8) and (5.54) for the true ground-state density ρ. This immediately leads to the expression

$$E_{xc}[\rho] = \frac{1}{2} \int d^3r\, d^3r'\, v(\underline{r},\underline{r}')\, \rho(\underline{r})\rho(\underline{r}')$$

$$+ \int d^3r\, v_{xc}^{(-)}(\underline{r})\rho(r) + i\hbar\, \mathrm{Tr}\{ \ln(1 - M_1 G_{10}) + M_1 G_{11} \} - i\, Y(1) , \qquad (5.55)$$

where we have used (5.18) for $E(0)$ and the definition of the KS-effective potential v_{eff}, which is [cf. (4.7), (3.7) and see (4.8)]

$$v_{eff}(\underline{r}) = u(\underline{r}) + \int d^3r'\, v(\underline{r},\underline{r}')\, \rho(\underline{r}') + v_{xc}^{(-)}(\underline{r}) . \qquad (5.56)$$

In order to write (5.55) in a more compact form it is advantageous to introduce two specific contributions to the first order function $Y^{(1)}(\lambda)$ of (5.49a) , namely

$$Y_a^{(1)}(\lambda) = \frac{1}{2}\,\mathrm{Tr}\{[\hbar(\sim) - \lambda\omega]\, G_{1\lambda}\}, \tag{5.57a}$$

and

$$Y_b^{(1)}(\lambda) = \frac{1}{2}\,\mathrm{Tr}\{\hbar\,(\bullet\!\!-\!\!\bigcirc)\, G_{1\lambda}\}. \tag{5.57b}$$

Following the rules for the evaluation of M-diagrams, these contributions can easily be evaluated at $\lambda = 1$: The contribution (5.57a) leads to[†)]

$$\begin{aligned} Y_a^{(1)}(1) &= \frac{1}{2}\,\mathrm{Tr}\{-2\omega G_{11}\} \\ &= -\int d^3r\, w(\underline{r})\, G_{11}(\underline{r}t, \underline{r}t^+) \\ &= -i\int d^3r d^3r'\, v(\underline{r},\underline{r}')\, \rho(\underline{r})\, \rho(\underline{r}') \\ &\quad - i\int d^3r\, v_{xc}^{(-)}(\underline{r})\, \rho(\underline{r}), \end{aligned} \tag{5.58}$$

where the last equality holds because of (5.56) and $\rho(\underline{r}) = -i\, G_{11}(\underline{r}t, \underline{r}t^+)$. The contribution (5.57b) equals

$$\begin{aligned} Y_b^{(1)}(1) &= -\frac{i}{2}\int d^3r d^3r'\, v(\underline{r},\underline{r}')\, G_{11}(\underline{r}t, \underline{r}t^+)\, G_{11}(\underline{r}'t', \underline{r}'t'^+) \\ &= \frac{i}{2}\int d^3r d^3r'\, v(\underline{r},\underline{r}')\, \rho(\underline{r})\, \rho(\underline{r}'). \end{aligned} \tag{5.59}$$

Since we have

$$\begin{aligned} -i\left\{(Y_a^{(1)}(1) + Y_b^{(1)}(1)\right\} &= -\frac{1}{2}\int d^3r d^3r'\, v(\underline{r},\underline{r}')\, \rho(\underline{r})\, \rho(\underline{r}') \\ &\quad - \int d^3r\, v_{xc}^{(-)}(\underline{r})\, \rho(\underline{r}), \end{aligned} \tag{5.60}$$

it is convenient to introduce the function

[†)] The notation t^+ stands for $t + \eta$, with $\eta > 0$ but infinitesimally small.

$$Y_{xc}(1) = Y(1) - \{Y_a^{(1)}(1) + Y_b^{(1)}(1)\}\ , \tag{5.61}$$

enabling us to write (5.55) in the form

$$E_{xc}[\rho] = i\hbar\, \mathrm{Tr}\{\ln(1 - M_1 G_{10}) + M_1 G_{11}\} - iY_{xc}(1)\,. \tag{5.62}$$

This is the desired expression for the exchange-correlation energy functional. In the next section we shall derive, with the help of (5.62) and (4.15), an expression for Δ_g which can in principle be used in actual calculations.

6. An expression for Δ_g in terms of the improper mass operator

In section 4 we derived an expression for the KS-gap correction in terms of the two functions $v_{xc}^{(+)}(\underline{r})$ and $v_{xc}^{(-)}(\underline{r})$. In view of the fact that both functions are derivatives of the exchange-correlation functional E_{xc} with respect to the density, we devoted the foregoing section to the derivation of an expression for E_{xc}. In this section we shall show how to take the functional derivatives, and end up with an expression for Δ_g in which , apart from the Kohn-Sham function $\psi_{N+1}(\underline{r};N)$, a mass-operator $\tilde{M}_1$ occurs which is closely related to M_1 introduced in section 5[4,11,17].

Let us suppose that the one-particle KS-equation (3.4) has been solved and that the corresponding complete set $\{\psi_j(\underline{r};N)\}$ of normalized one-electron wave functions is available. Then the KS-Green function G_{10} satisfying (5.28) can be expanded in terms of ψ_j's as

$$G_{10}(\underline{r}_1 t_1, \underline{r}_2 t_2) = -i\{\theta(t_1 - t_2) \sum_{j=N+1}^{\infty} \psi_j(\underline{r}_1;N)\psi_j^*(\underline{r}_2;N)$$

$$\times \exp[-i\varepsilon_j(N)(t_1-t_2)/\hbar] - \theta(t_2 - t_1) \sum_{j=1}^{N} \psi_j^*(\underline{r}_2;N)\psi_j(\underline{r}_1;N)$$

$$\times \exp[+i\varepsilon_j(N)(t_2-t_1)/\hbar]\} \ . \qquad (6.1)$$

This expression can be obtained by starting from the definition (5.27), using the completeness of the eigenstates of $\tilde{H}_o$ and applying equations (5.16) and (5.17). It follows from (6.1) that

$$G_{10}(\underline{r}t, \underline{r}t^+) = i \sum_{j=1}^{N} |\psi_j(\underline{r};N)|^2$$

$$= i\,\rho_N(\underline{r};N), \qquad (6.2)$$

where $t^+ \triangleq (t+\eta)_{\eta\downarrow 0}$. The last equality in (6.2) holds because of (3.14). A change $\delta\rho_{N+1}(\underline{r};N)$, (see (4.10)), in density corresponds to a change in G_{10} given by

$$\delta_+ G_{10}(\underline{r}t, \underline{r}'t') = i\,\psi_{N+1}(\underline{r};N)\ \psi_{N+1}^*(\underline{r}';N)$$

$$\times \exp\,[-i\,\varepsilon_{N+1}(N)(t-t')/\hbar] \ , \qquad (6.3)$$

or, in the Fourier energy domain,

$$\delta_+ G_{10}(\underline{r},\underline{r}';\varepsilon) = \int d(t-t')\ \exp[+i\varepsilon(t-t')\sim/\hbar]$$

$$\times \delta_+ G_{10}(\underline{r}t,\underline{r}'t')$$

$$= 2\pi i\hbar\ \delta(\varepsilon-\varepsilon_{N+1}^{(N)})\psi_{N+1}(\underline{r};N)\psi_{N+1}^{*}(\underline{r}';N)\,. \tag{6.4}$$

As a result of the density variation $\delta\rho_{N+1}(N)$, the exchange-correlation energy functional will vary. Denoting the *linear* variation of E_{xc}, as a result of $\delta\rho_{N+1}(N)$, by $\delta_+ E_{xc}$, we obtain from (5.62), using $(1 - M_1 G_{10})^{-1} = G_{10}^{-1}G_{11}$ (see (5.52)), and $(1- M_1 G_{10}) = G_{11}^{-1}G_{10}$,

$$\delta_+ E_{xc} = i\hbar\ \mathrm{Tr}\ \{(G_{10}^{-1}G_{11})[(\delta_+ G_{11}^{-1})G_{10} + G_{11}^{-1}(\delta_+ G_{10})]$$

$$+ (\delta_+ M_1)G_{11} + M_1(\delta_+ G_{11})\} - i\,\delta_+ Y_{xc}(1)\,. \tag{6.5}$$

Owing to the cyclical property of the trace, this reduces to

$$\delta_+ E_{xc} = i\hbar\ \mathrm{Tr}\{(\delta_+ G_{11}^{-1})G_{11}+G_{10}^{-1}(\delta_+ G_{10}) + (\delta_+ M_1)G_{11}+M_1(\delta_+ G_{11})\}$$

$$- i\delta_+ Y_{xc}(1)\,. \tag{6.6}$$

According to (4.14) we can write the *linear* variation of E_{xc} as

$$\delta_+ E_{xc} = \mathrm{Tr}\{\frac{\delta E_{xc}}{\delta\rho(\underline{r})}\Big|_{\rho=\rho_{N+1}(N)}\ \delta\rho_{N+1}(N)\}$$

$$= \mathrm{Tr}\{\nu_{xc}^{(+)}\ \delta\rho_{N+1}(N)\}\,. \tag{6.7}$$

From (5.49) one can readily obtain

$$\frac{\delta Y^{(\nu)}(\lambda)}{\delta G_{1\lambda}} = \hbar M_\lambda^{(\nu)}\ ,\ \nu = 1,2,3,\ldots\ . \tag{6.8}$$

The case $\nu = 1$ can be directly verified from (5.49a), whereas the case $\nu > 1$ is arrived at by making use of (5.49b), the structure of $M_\lambda^{(\nu)}$ in terms of Green functions $G_{1\lambda}$, and the cyclical property of the trace (compare also with the discussion between (5.43) and (5.44)). By defining the exchange correlation mass operator M_{xc} by

$$M_{xc}(1,2) = \hbar^{-1} \frac{\delta Y_{xc}(1)}{\delta G_{11}(2,1)} , \tag{6.9}$$

we immediately obtain from (6.8), (5.61), (5.58) and (5.59)

$$\hbar M_{xc}(1,2) = \hbar M_1(1,2) - \left\{-w(\underline{r}_1) + v_H(\underline{r}_1)\right\}\delta(1,2), \tag{6.10}$$

which, according to (4.7) and (5.11), can be written as

$$M_{xc}(1,2) = M_1(1,2) + \hbar^{-1} v_{xc}^{(-)}(\underline{r}_1)\delta(1,2). \tag{6.11}$$

Rewriting (6.9) in the form $\delta Y_{xc}(1) = \mathrm{Tr}\{\hbar M_{xc}\delta G_{11}\}$ we can write, according to (6.11),

$$\delta_+ Y_{xc}(1) = \mathrm{Tr}\{\hbar M_1 \delta_+ G_{11}\} + \mathrm{Tr}\{\tilde{v}_{xc}^{(-)}\ \delta_+ G_{11}\}, \tag{6.12}$$

where

$$\tilde{v}_{xc}^{(-)}(1,2) = v_{xc}^{(-)}(\underline{r}_1)\delta(1,2). \tag{6.13}$$

Since the Kohn-Sham density $\rho_N(\underline{r};N)$ is exact, we have, in view of (6.2),

$$\begin{aligned}\rho_N(\underline{r};N) &= -iG_{10}(\underline{r}t,\underline{r}t^+) \\ &= -iG_{11}(\underline{r}t,\underline{r}t^+).\end{aligned} \tag{6.14}$$

Therefore, the last term in the right-hand side of (6.12) can be replaced by $i\mathrm{Tr}\{v_{xc}^{(-)}\delta\rho_{N+1}(N)\}$ which results in

$$\delta_+ Y_{xc}(1) = \mathrm{Tr}\{\hbar M_1 \delta_+ G_{11}\} + i\,\mathrm{Tr}\{\nu_{xc}^{(-)} \delta\rho_{N+1}(N)\} \ . \tag{6.15}$$

By combining (6.6), (6.7) and (6.15), we now arrive at

$$\mathrm{Tr}\{(\nu_{xc}^{(+)} - \nu_{xc}^{(-)})\ \delta\rho_{N+1}(N)\}$$

$$= i\hbar\mathrm{Tr}\{(\delta_+ G_{11}^{-1})G_{11} + G_{10}^{-1}(\delta_+ G_{10}) + (\delta_+ M_1)G_{11}\} \ . \tag{6.16}$$

Since Δ_g can be written [see (4.10) and (4.15)]

$$\Delta_g = \int d^3r\ \psi_{N+1}^*(\underline{r};N)\left\{\nu_{xc}^{(+)}(\underline{r};N) - \nu_{xc}^{(-)}(\underline{r};N)\right\}\psi_{N+1}(\underline{r};N)$$

$$= \mathrm{Tr}\left\{\left(\nu_{xc}^{(+)} - \nu_{xc}^{(-)}\right)\delta\rho_{N+1}(N)\right\} \ , \tag{6.17}$$

the gap correction can be expressed as

$$\Delta_g = i\hbar\ \mathrm{Tr}\ \{(\delta_+ G_{11}^{-1})G_{11} + G_{10}^{-1}(\delta_+ G_{10}) + (\delta_+ M_1)G_{11}\}. \tag{6.18}$$

From an implication of the Dyson equation (5.30), $G_{11}^{-1} = G_{10}^{-1} - M_1$, it follows that we may substitute

$$\delta_+ G_{11}^{-1} = \delta_+ G_{10}^{-1} - \delta_+ M_1 \tag{6.19}$$

in (6.18), which yields

$$\Delta_g = i\hbar\ \mathrm{Tr}\ \{(\delta_+ G_{10}^{-1})G_{11} + G_{10}^{-1}(\delta_+ G_{10})\} \ . \tag{6.20}$$

By introducing the *improper* mass operator $\tilde{M}_1$ through the equation

$$G_{11} = G_{10} + G_{10}\tilde{M}_1 G_{10} \ , \tag{6.21}$$

and using

$$\delta_+ G_{10}^{-1} = - G_{10}^{-1} (\delta_+ G_{10}) G_{10}^{-1} , \tag{6.22}$$

(which follows from $\delta_+(G_{10}^{-1}G_{10}) = \delta_+(1) = 0$) we can write (6.20) in the form

$$\Delta_g = - i\hbar \, \mathrm{Tr}\{\tilde{M}_1 \delta_+ G_{10}\}$$

$$= - i\hbar \int d^3 r_1 \int d(1') \, \tilde{M}_1(1,1') \, \delta_+ G_{10}(1',1^+) . \tag{6.23}$$

It should be noted that, owing to the equations (5.30) and (5.51), $\tilde{M}_1$ and M_1 are related according to

$$\tilde{M}_1 = M_1 (1 - G_{10} M_1)^{-1}$$

$$= (1 - M_1 G_{10})^{-1} M_1$$

$$= M_1 + M_1 G_{10} M_1 + M_1 G_{10} M_1 G_{10} M_1 + \cdots \quad . \tag{6.24}$$

Using the Fourier integral representations

$$\tilde{M}(\underline{r}t, \underline{r}'t') = \int \frac{d\varepsilon}{2\pi\hbar} \, \tilde{M}(\underline{r}, \underline{r}'; \varepsilon) \exp[i\varepsilon(t-t')/\hbar] , \tag{6.25}$$

$$\delta_+ G_{10}(\underline{r}'t, \underline{r}t^+) = \int \frac{d\varepsilon'}{2\pi\hbar} \, \delta_+ G_{10}(\underline{r}', \underline{r}; \varepsilon') \exp[i\varepsilon'(t'-t^+)/\hbar] , \tag{6.26}$$

we obtain for (6.23)

$$\Delta_g = -i \int d^3 r_1 d^3 r_1' \int \frac{d\varepsilon}{2\pi} \, \tilde{M}(\underline{r}_1, \underline{r}'; \varepsilon) \delta_+ G_{10}(\underline{r}_1', \underline{r}_1; \varepsilon)$$

$$\times \exp[-i\varepsilon \, 0^+/\hbar] . \tag{6.27}$$

Here, use has been made of the relations

$$\int dt_1' \exp[i(\varepsilon-\varepsilon')(t_1-t_1')/\hbar] = 2\pi\hbar\,\delta(\varepsilon-\varepsilon'), \tag{6.28}$$

and

$$\int d\varepsilon\ \delta(a\varepsilon)\ f(\varepsilon) = \frac{1}{|a|} f(0). \tag{6.29}$$

From (6.4), (6.23) and (6.27) we finally arrive at the desired result

$$\Delta_g = \hbar \int d^3r d^3r'\ \psi^*_{N+1}(\underline{r};N)\ \tilde{M}_1(\underline{r},\underline{r}';\varepsilon_{N+1}(N))\ \psi_{N+1}(\underline{r}';N) \tag{6.30}$$

The simplicity of (6.30) is striking. Its derivation, however, turned out to be very lengthy. We have managed to present a derivation which works, albeit at the expence of introducing many notations, functions and quantities, which in the future may turn out to be of little use. On the other hand, this is, paradoxally, also the advantage of the present work: All notions, functions, functionals etc. that have been introduced in the overwhelming amount of literature available on this subject have been discussed and put together in a coherent way.

Appendix A

Functional derivative

This appendix is meant to present as much of the theory of functional derivatives[18-20] as is necessary in the context of the present work.

Let us consider a functional $F[\phi]$. We define the functional derivative, $\delta F[\phi]/\delta\phi(x)$, by means of the relation

$$\int dx \frac{\delta F[\phi]}{\delta\phi(x)} f(x) = \lim_{\eta\to 0} \frac{1}{\eta} \{F[\phi + \eta f] - F[\phi]\}, \tag{A1}$$

where $f(x)$ is an arbitrary but smooth and integrable function.

From the definition it is quite easy to see that functional differentiation has the usual properties satisfied by ordinary differentiation, that is,

$$\frac{\delta}{\delta\phi(x)} a = 0, \tag{A2}$$

$$\frac{\delta}{\delta\phi(x)} \{aF_1[\phi] + bF_2[\phi]\} = a \frac{\delta F_1[\phi]}{\delta\phi(x)} + b \frac{\delta F_2[\phi]}{\delta\phi(x)}, \tag{A3}$$

$$\frac{\delta}{\delta\phi(x)} F_1[\phi]F_2[\phi] = \frac{\delta F_1[\phi]}{\delta\phi(x)} F_2[\phi] + F_1[\phi] \frac{\delta F_2[\phi]}{\delta\phi(x)}, \tag{A4}$$

where F_1 and F_2 are functionals of ϕ, and a and b arbitrary functions independent of ϕ.

Let us consider some simple examples. For the functional $F[\phi] = \int dx\, u(x)\phi(x)$ we have

$$\int dx \frac{\delta F[\phi]}{\delta\phi(x)} f(x) = \lim_{\eta\to 0} \frac{1}{\eta} \{\int dx\, u(x) [\phi(x) + \eta f(x)]$$

$$- \int dx\, u(x)\phi(x)\} = \int dx\, u(x) f(x). \tag{A5}$$

Since this relation holds for any arbitrary f, one obtains

$$\frac{\delta}{\delta\phi(x)} \int dx'\, u(x')\, \phi(x') = u(x). \tag{A6}$$

For the functional $F[\phi] = \phi(x_o)$ we have

$$\int dx \frac{\delta F[\phi]}{\delta\phi(x)} f(x) = \lim_{\eta\to 0} \frac{1}{\eta} \{\phi(x_o) + \eta f(x_o) - \phi(x_o)\} = f(x_o), \tag{A7}$$

which implies the differentiation rule

$$\frac{\delta}{\delta\phi(x)} \phi(x_o) = \delta(x - x_o), \tag{A8}$$

where $\delta(x - x_o)$ is the Dirac δ-function.

In the above-given examples we have dealt only with *linear* functionals of ϕ. In such cases the derivatives are independent of ϕ, implying that higher-order derivatives vanish. However, for functionals depending non-linearly on ϕ, we can also define higher-order derivatives in a way analogous to ordinary derivatives. For instance, the second order derivative is defined by

$$\int dx dx' \frac{\delta^2 F[\phi]}{\delta\phi(x)\delta\phi(x')} f(x)\, g(x') = \lim_{\substack{\eta\to 0 \\ \eta'\to 0}} \frac{1}{\eta\eta'} \{ F[\phi + \eta f + \eta' g] - F[\phi + \eta f] - F[\phi + \eta' g] + F[\phi]\} . \tag{A9}$$

For $F[\phi] = \{\phi(x_o)\}^2$, the definition immediately gives us

$$\frac{\delta^2}{\delta\phi(x)\delta\phi(x')} \{\phi(x_o)\}^2 = 2\delta(x - x_o)\delta(x' - x_o). \tag{A10}$$

It is worth noting that by utilizing the above concept of functional derivative, we can expand a certain class of functionals, which we call "analytic functionals", in a Taylor-type of series,

$$F[\phi_1] = F[\phi_o] + \frac{1}{1!} \int dx \left.\frac{\delta F[\phi]}{\delta\phi(x)}\right|_{\phi = \phi_o} \{ \phi_1(x) - \phi_o(x) \}$$

$$+ \frac{1}{2!} \int dxdx' \left.\frac{\delta^2 F[\phi]}{\delta\phi(x)\delta\phi(x')}\right|_{\phi=\phi_o} \{\phi_1(x) - \phi_o(x)\}\{\phi_1(x') - \phi_o(x')\} + \ldots \quad . \tag{A11}$$

Appendix B

Diagrammatic approach to the calculation of the Green function and mass operator

This appendix is meant to recapitulate the main features of the diagrammatic approach to the one-particle Green function and the related mass operator for a many-particle system with interaction between the particles. The method carefully accounts for all perturbation expansion terms when expanding the full Green function G_1 in terms of some "unperturbed" Green function G_1^o . The diagrammatic technique, originally due to Feynman, enables one to consider the whole perturbation series merely on the basis of topological properties of diagrams.

Let the Hamiltonian of the many-particle system under consideration be

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \tag{B1}$$

where the "unperturbed" Hamiltonian is given by

$$\hat{H}_0 = \hat{T} + \hat{U} + \hat{Z}, \tag{B2}$$

and the "perturbation" Hamiltonian by

$$\hat{H}_1 = \hat{V} - \hat{Z} . \tag{B3}$$

In second-quantization notation we have

$$\hat{T} = \int d^3r\, \hat{\psi}^{\dagger}(\underline{r}) \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \hat{\psi}(\underline{r}), \tag{B4a}$$

$$\hat{U} = \int d^3r\, \hat{\psi}^{\dagger}(\underline{r})\, u(\underline{r})\, \hat{\psi}(\underline{r}), \tag{B4b}$$

$$\hat{Z} = \int d^3r\, \hat{\psi}^{\dagger}(\underline{r})\, z(\underline{r})\, \hat{\psi}(\underline{r}), \tag{B4c}$$

$$\hat{V} = \tfrac{1}{2} \int d^3r d^3r'\, \hat{\psi}^{\dagger}(\underline{r})\, \hat{\psi}^{\dagger}(\underline{r}')\, v(\underline{r},\underline{r}')\, \hat{\psi}(\underline{r}')\, \hat{\psi}(\underline{r}) . \tag{B4d}$$

Here it has been assumed that $v(\underline{r},\underline{r}') = v(\underline{r}',\underline{r})$, while $\hat{\psi}^{\dagger}(\underline{r})$ and $\hat{\psi}(\underline{r})$ are creation and annihilation field operators, respectively, in the Schrödinger picture . The operator $\hat{z}$ has been introduced in order to anticipate on "local parts" in the perturbation operator $\hat{V}$. Its introduction is in the spirit of the local density functional formalism, but it is not obligatory.

The one-particle Green function $G_1(1,2)$ is defined by

$$G_1(1,2) = -i\ {}_H\langle\Psi_0|T_w[\hat{\psi}_H(1)\ \hat{\psi}_H^{\dagger}(2)]|\Psi_0\rangle_H \tag{B5}$$

where $|\Psi_0\rangle_H$ is the normalized ground state of the interacting system, and $\hat{\psi}_H^{\dagger}$, $\hat{\psi}_H$ are the creation and annihilation field operators, all in the Heisenberg representation. The arguments j with j = 1,2 stand for the space-time point $(\underline{r}_j,t_j)$. The time-ordering operator T_w has been defined in (5.25). In the absence of interaction, $G_1(1,2)$ reduces to the "unperturbed" Green function

$$G_1^{o}(1,2) = -i\ {}_I\langle\Phi_0|T_w[\hat{\psi}_I(1)\hat{\psi}_I^{\dagger}(2)]|\Phi_0\rangle_I. \tag{B6}$$

Note that the state $|\Psi_0\rangle_H$ in (B5) has been replaced by the unperturbed normalized ground state $|\Phi_0\rangle_I$ $(=|\Phi_0\rangle_H)$, while the Heisenberg operators $\hat{\psi}_H^{\dagger}$, $\hat{\psi}_H$ in (B5) are reduced to the interaction representation operators

$$\hat{\psi}_I^{\dagger}(1) = \exp(i\hat{H}_0 t_1/\hbar)\ \hat{\psi}^{\dagger}(\underline{r}_1)\exp(-i\ \hat{H}_0 t_1/\hbar), \tag{B7a}$$

$$\hat{\psi}_I(1) = \exp(i\hat{H}_0 t_1/\hbar)\ \hat{\psi}(\underline{r}_1)\ \exp(-i\ \hat{H}_0 t_1/\hbar). \tag{B7b}$$

Starting from the equation of motion, $i\hbar\,\partial\hat{\psi}_I(\underline{r}_1 t_1)/\partial t_1 = [\hat{\psi}_I(\underline{r}_1 t_1),\ \hat{H}_0]$, it is easily shown that $G_1^{o}(1,2)$ satisfies

$$\left[i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla_1^2 - u(\underline{r}_1) - z(\underline{r}_1)\right] G_1^{o}(1,2) = \hbar\,\delta(1,2). \tag{B8}$$

Similarly, by starting from the equation of motion, $i\hbar\partial\hat{\psi}_H(\underline{r}_1 t_1)/\partial t_1 = [\hat{\psi}_H(\underline{r}_1 t_1),\ \hat{H}]$, one obtains

$$\left[i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla_1^2 - u(\underline{r}_1) - z(\underline{r}_1)\right] G_1(1,2) + i\int d(3)\upsilon(1,3)G_2(13;23^{+}) = \hbar\,\delta(1,2). \tag{B9}$$

Here the two-particle Green function

$$G_2(12;34) = (-i)^2 \; {}_H\langle \Psi_0 \,|\, T_w[\hat{\psi}_H(1)\; \hat{\psi}_H(2)\; \hat{\psi}_H^{\dagger}(3)\; \hat{\psi}_H^{\dagger}(4)\,]\,|\Psi_0\rangle_H \tag{B10}$$

has been introduced, while $v(1,3)$ stands for $v(\underline{r}_1,\underline{r}_3)\delta(t_1-t_3)$. We may, in this stage introduce the *mass operator* M through its defining equation

$$i\int d(3)\; v(1,3)\; G_2(13;23^+) = -\hbar\int d(3)\; M(1,3)G_1(3,2), \tag{B11}$$

and arrive at the alternative equation of motion for G_1 [cf. (5.26)]

$$[i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m} - u(\underline{r}_1) - z(\underline{r}_1)]\; G_1(1,2) = \hbar\,\delta(1,2) + \hbar\int d(3)M(1,3)G_1(3,2). \tag{B12}$$

In this way the use of a multi-particle Green function, such as in (B10) can be circumvented at the cost of, however, the introduction of a (complicated) mass-operator M. One can formally write (B8) as

$$G_1^o(1,2) = \hbar\,[i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla_1^2 - u(\underline{r}_1) - z(\underline{r}_1)]^{-1}\delta(1,2)\;. \tag{B13}$$

Hence, if we write the last term in the right-hand side of (B12) alternatively as

$$\hbar\int d(3)\; M(1,3)\; G_1(3,2) = \hbar\int d(3)\; d(4)\; \delta(1,3)\; M(3,4)\; G_1(4,2), \tag{B14}$$

and multiply (B12) on the left with $[i\hbar\frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m}\nabla_1^2 - u(\underline{r}_1) - z(\underline{r}_1)\;]^{-1}$, we directly obtain an inhomogeneous integral equation of the second kind for G_1, usually referred to as Dyson's equation:

$$G_1(1,2) = G_1^o(1,2) + \int d(3)\; d(4)\; G_1^o(1,3)\; M(3,4)\; G_1(4,2), \tag{B15a}$$

or symbolically

$$G_1 = G_1^o + G_1^o M G_1. \tag{B15b}$$

It can directly be verified that

$$G_1 = (1 - G_1^o M)^{-1} G_1^o$$

$$= G_1^o + G_1^o M G_1^o + G_1^o M G_1^o M G_1^o + \ldots , \qquad (B16)$$

satisfies (B15), and as such is a formal solution of (B15) (or (B12)). The above mass operator is often called the *proper* mass operator. One may also introduce the *improper* mass operator $\tilde{M}$ defined by

$$\tilde{M} = M\, G_1 G_1^{o-1}$$

$$= M + M\, G_1^o M + M G_1^o M\, G_1^o M + \ldots , \qquad (B17)$$

such that the Dyson equation can be written as

$$G_1 = G_1^o + G_1^o \tilde{M} G_1^o . \qquad (B18)$$

In Fig. B1 a diagrammatic notation of Eqs. (B15)-(B18) has been given. It should be realized that these diagrammatic equations are nothing but formal visualizations of the respective equations and do not at this stage contribute to solving G_1 and M in terms of G_1^o.

The general theory[21] shows that G_1 can be written in the form

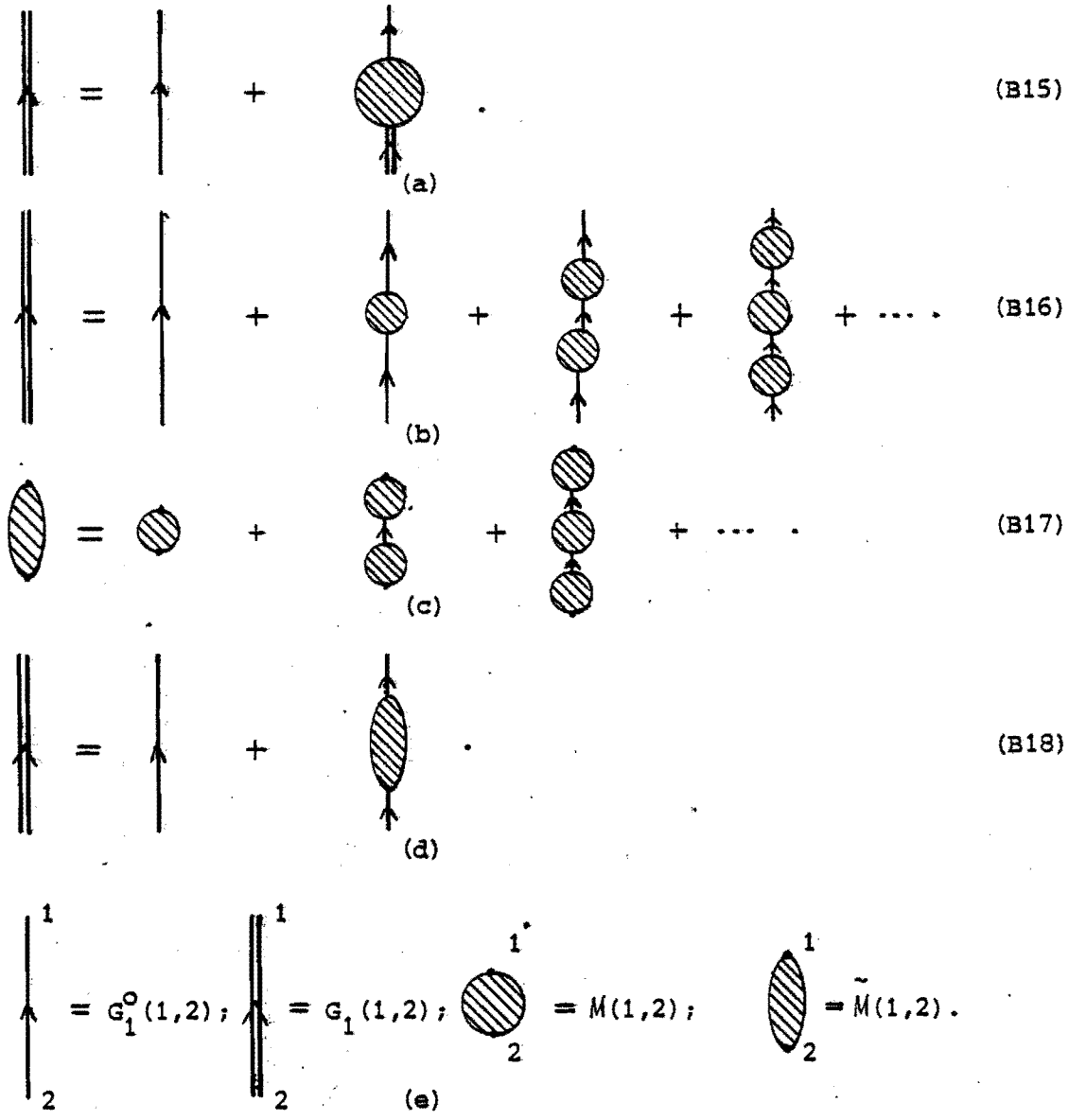
$$G_1(1,2) = -i \sum_{N=0}^{\infty} \left(\frac{-i}{\hbar}\right)^n \frac{1}{n!} \{ \int_{-\infty}^{\infty} dt_1' \ldots \int_{-\infty}^{\infty} dt_n'$$

$$\times {}_I\langle \Phi_0 | T_w [\tilde{H}_I(t_1') \ldots \tilde{H}_I(t_n')\, \tilde{\psi}_I(1)\, \tilde{\psi}_I^{\dagger}(2)] | \Phi_0 \rangle_I \}_L \qquad (B19)$$

where the subscript L indicates that only some "appropriate" terms of a specific series expansion of the term within the braces are to be accounted for. This series expansion as well as the condition for a term to be "appropriate" will be specified below. In (B19), $\tilde{H}_I$ stands for the perturbation Hamiltonian $\tilde{H}_1$ in the interaction representation. It can be written as

$$\hat{H}_I(t_1) = \frac{1}{2}\int d^3r_1 d(2)\ \hat{\psi}_I^\dagger(1)\ \hat{\psi}_I^\dagger(2)\ v(1,2)\ \hat{\psi}_I(2)\ \hat{\psi}_I(1)$$

$$- \int d^3r_1\ \hat{\psi}_I^\dagger(1)\ z(\underline{r}_1)\ \hat{\psi}_I(1). \qquad \text{(B20)}$$



(B15)

(B16)

(B17)

(B18)

Fig.B1 Diagrammatic notation of Eqs. (B15)-(B18), in terms of symbols which are defined in (e).

It can be shown[22], by making use of Wick's theorem, that the time integration of the expectation value of the time-ordered field operators

may be replaced by a multiple space-time integral of a series of products of unperturbed Green functions G_1°, interaction functions $U(x_j,x_j')$ and $-z(\underline{r}_k)$, and a numerical factor to be specified below. However, only those products are allowed which do not fall apart into factors depending on disjunct subsets of the $(\underline{r}_j,t_j)$ variables. Products that do fall apart in this sense are "inappropriate" and do not contribute to (B19). The "appropriate" terms are called *linked* (note the index L for "linked" in (B19)) or *connected*. Each term of the above series can be represented uniquely by a so-called Feynman diagram, of which only the *linked* (or connected) ones contribute to G_1. A diagram is said to be linked, if it does not fall into separate parts (see Fig.(B2)). A Feynman diagram representing a term with n interactions U or $-z$ is called a diagram of nth-order. The prescription of drawing an nth-order diagram involving m U-interactions and (n-m) $-z$-interactions is as follows:

(1) Mark 2m points (vertices) on the paper and label them $x_1,x_2,\ldots x_m$ and $x_1', x_2', \ldots, x_m'$, respectively. Join the pairs of points (x_j,x_j'), $j = 1,2,\ldots,m$, by U-interaction lines (broken lines ----). Mark (n-m) additional points x_j, $j = m+1, \ldots, n$, and join to each one a $-z$-interaction line (wavy line ∿∿∿∿).

(ii) Mark two extra points x and y and call them *external* points (x_j's and x_j''s are called internal points).

(iii) Draw *directed* lines (full lines ⟶), representing unperturbed Green functions G_1°, such that each of the n+m internal points has precisely one line entering and one line leaving it, and such that x has only a line entering and y has only a line leaving it. In this way one has m U-lines, (n-m) $-z$-lines, and (n+m-1)+2 = n+m+1 "particle" lines (full lines).

As an example, consider Fig. B2 representing two 3rd-order diagrams.

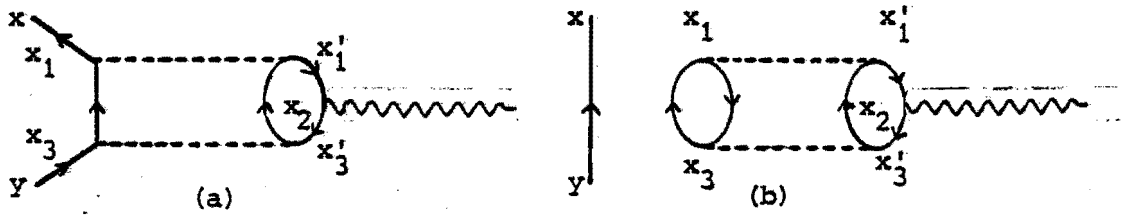


Fig.B2. Examples of two 3rd-order Feynman diagrams. (a) This diagram is called *linked* or connected diagram. (b) This diagram is called an *unlinked* diagram.

In considering diagrams, we have to restrict ourselves to the collection of *topologically inequivalent* diagrams only[23]. Two diagrams are said to be *topologically equivalent* if they can be transformed into one another, irrespective of the names of the vertices, by a continuous deformation. By continuous deformation of a diagram we mean all kinds of rotations, either of the whole or a part of the diagram, stretchings, shortenings, etc., provided that none of the lines is cutted. For instance, the diagrams in Fig. B3 are all topologically equivalent.

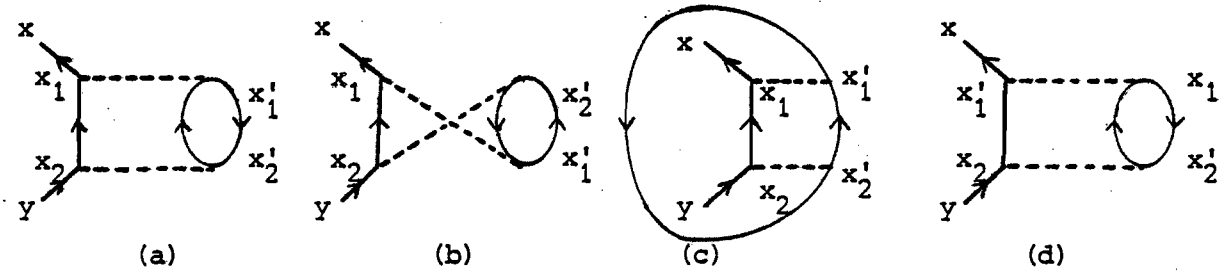


Fig. B3. Four 2nd-order diagrams which are topologically equivalent with each other.

We may call a representative of a class of topological equivalent diagrams, the *topological structure* of the corresponding class. The topological structures contributing to G_1, up to the second order are given in Fig.B4.

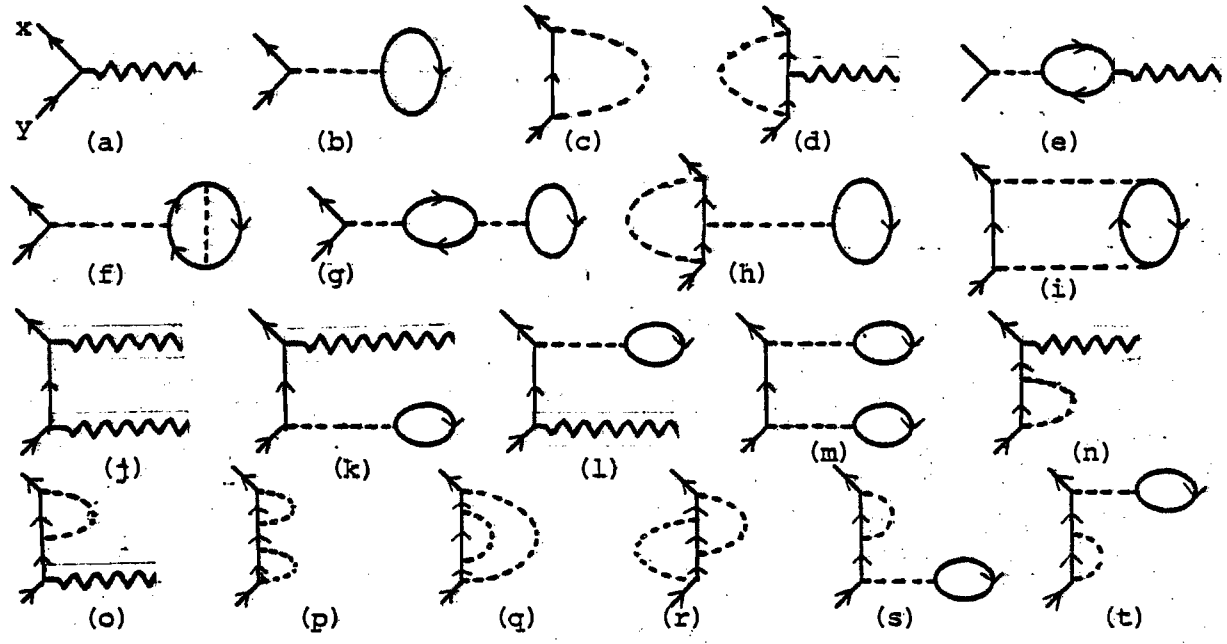


Fig.B4. All linked topological structures contributing to G_1, up to the second order. (a), (b) and (c) are 1st-order structures; (d)-(t) are 2nd-order structures.

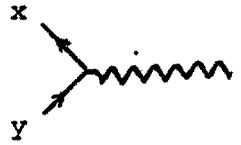
The prescription of calculating the contribution of a given topological structure of nth-order, with m υ-lines and (n-m) -z-lines, to the full Green function is given below.

(i) Assign to each υ-line connecting x_j and x_j', $\upsilon(x_j,x_j')$; to each-z-line in x_k, $-z(x_k)$; and to each full line directed from $x_j^{(')}$ to $x_k^{(')}$, $G_1^o(x_k^{(')}, x_j^{(')})$, where $x_j^{(')}$ stands for aither x_j or x_j'. In the case $x_k^{(')} \equiv x_j^{(')}$, it has to be assumed that $x_j^{(')} = x_k^{(')+}$.

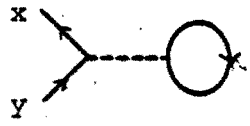
(ii) Multiply the contribution of all lines in the diagram, and subsequently integrate over all *internal* variables $x_j^{(')}$, $x_k^{(')}$, etc.

(iii) Multiply the result obtained in (ii) by a factor $(-i)(-i/\hbar)^n(i)^{n+m+1} \times(-1)^F = (-1)^F i^m/\hbar^n$. Here F is the number of *closed loops* in the diagram. For example F's in the diagrams (c), (f) and (g) of Fig. B4 are 0,1 and 2, respectively.

As an example, we write down the contribution to G_1 of the topological structures (a) and (b) in Fig. B4,



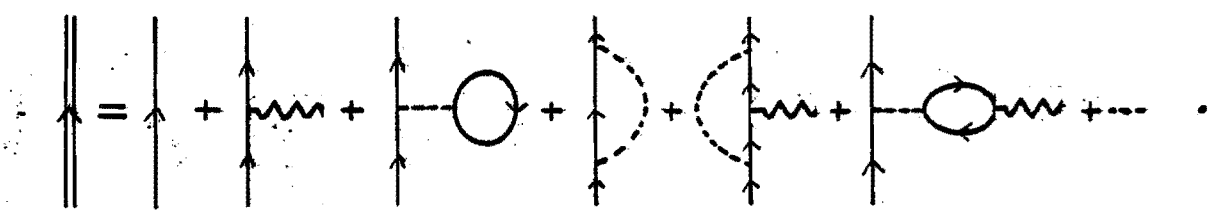
$$= -\frac{1}{\hbar}\int dx_1 G_1^o(x,x_1)\, z(\underline{r}_1)\, G_1^o(x_1,y). \tag{B22}$$



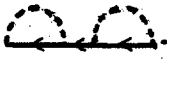
$$= (-1)\frac{i}{\hbar}\int dx_1 dx_1' G_1^o(x,x_1)\, \upsilon(x_1,x_1') G_1^o(x_1',x_1'^+)\; G_1^o(x_1,y)$$

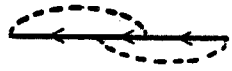
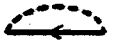
$$= \frac{-i}{\hbar}\int dx_1 d^3r_1' G_1^o(x,x_1)\, v(\underline{r}_1,\underline{r}_1')\; G_1^o(\underline{r}_1' t_1, \underline{r}' t_1^+)\, G_1^o(x_1,y). \tag{B23}$$

We are now able to obtain G_1 in terms of G_1^o, υ and -z, in the form of a diagrammatic expression



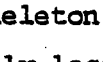
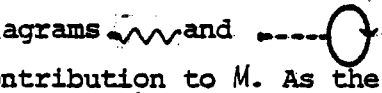
By comparing this expansion with the ones in Fig. B1, it is also possible to express the proper and improper mass operators M and $\tilde{M}$ in terms of diagrams involving G_1^o, υ and $-z$:

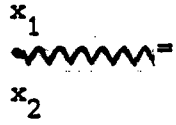
Let us consider a diagram contrubiting to G_1 with external lines left out (i.e. without the particle lines connected with x and y). If such a diagram *cannot* be split up into two separate pieces by cutting only one particle line, the diagram contributes to the proper mass-operator M. The collection of all diagrams to be obtained in this way gives the complete proper mass-operator. The complete set of these diagrams and of the remaining diagrams (that can be split up into separate pieces) give the improper mass-operator $\tilde{M}$. As an example take the two diagrams  and  . The first one is proper and contributes to M, the second one is improper; both diagrams contribute to $\tilde{M}$. Leaving out in Fig. B4 all external lines, the remaining diagrams make up the total contribution, up to the second order, of the improper mass-operator $\tilde{M}$.

Let us now introduce the concept of *skeleton* M-diagrams[24]: Such a diagram is defined by demanding that it is an M-diagram with the restriction that it does not "contain" any internal M-diagram. For example  is a skeleton M-diagram whereas  is not, for it "contains"  . It will be clear that all diagrams for M may be obtained by drawing all skeleton M-diagrams and then inserting all possible M-parts. This is equivalent with[24,25]

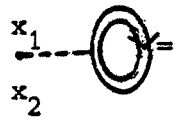
$$M = \{\text{Contribution of all possible skeleton } M\text{-diagrams with } G_1^o \text{ replaced by } G_1\}. \qquad \text{(B24)}$$

Equation (B24) is actually an implcit equation for M since G_1 also contains M.

In considering the skeleton M-diagrams we notice that the two first-order skeleton M-diagrams  and  are special ones as they represent the only local contribution to M. As the mass-operator, introduced in (B11), is by definition a two point function, it turns out that in these two cases the M-contributions are to be expressed with the help of δ-functions [cf. (B22) and (B23)]:

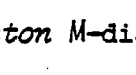


$$= -\frac{1}{\hbar}\ \delta(x_1,x_2)\, z(\underline{r}_1)\,, \tag{B25}$$



$$= \frac{-i}{\hbar}\ \delta(x_1,x_2) \int d^3r_1'\ v(\underline{r}_1,\underline{r}_1')\ G_1(\underline{r}_1't_1',\underline{r}_1't_1'^{+})\ . \tag{B26}$$

Note that a (double) full line in (B26) represents a G_1-function (see also Fig. B1e) in agreement with (B24).

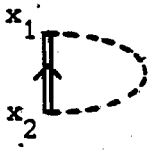
Below we present the prescription of calculating the contribution of *skeleton* M-diagrams of order n ( excluded).

(i) Assign to each U-line connecting x_j and x_j', $U(x_j,x_j')$, and to each (double) full line ⟹ directed from $x_j^{(')}$ to $x_k^{(')}$ $G_1(x_k^{(')}, x_j^{(')})$.

(ii) Multiply the contribution of all lines in the diagram, and subsequently integrate over all internal space-time variables except the ones connected with one particle line only.

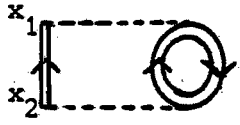
(iii) Multiply the result obtained in (ii) by the factor $(-i)(-i/\hbar)^n (i)^{2n+1} \times (-1)^F = (-1)^F (i/\hbar)^n$, F being the number of closed particle *loops* in the diagram.

As an example we give the contribution of the skelton M-diagrams  and  .



$$= \frac{i}{\hbar}\ v(\underline{r}_1,r_2)\ \delta(t_1-t_2)\ G_1(x_1,x_2)$$

$$= \frac{i}{\hbar}\ v(\underline{r}_1,\underline{r}_2)\ \delta(t_1-t_2)\ G_1(\underline{r}_1t_1,\underline{r}_2t_1^{+})\,. \tag{B27}$$



$$= (-1)\ \left(\frac{i}{\hbar}\right)^2 \int dx_1'dx_2'\ U(x_1,x_1')G_1(x_1',x_2')\ G_1(x_2',x_1')$$

$$\times U(x_2',x_2)\ G_1(x_1,x_2)$$

$$= \frac{1}{\hbar^2} \int d^3r_1'd^3r_2'\ v(\underline{r}_1,\underline{r}_1')\ G_1(\underline{r}_1't_1,\underline{r}_2't_2)\ G_1(\underline{r}_2't_2,\underline{r}_1't_1)$$

$$\times v(\underline{r}_2',\underline{r}_2)\ G_1(x_1,x_2)\,. \tag{B28}$$

In Fig. B5 the skeleton M-structures up to the third order are presented.

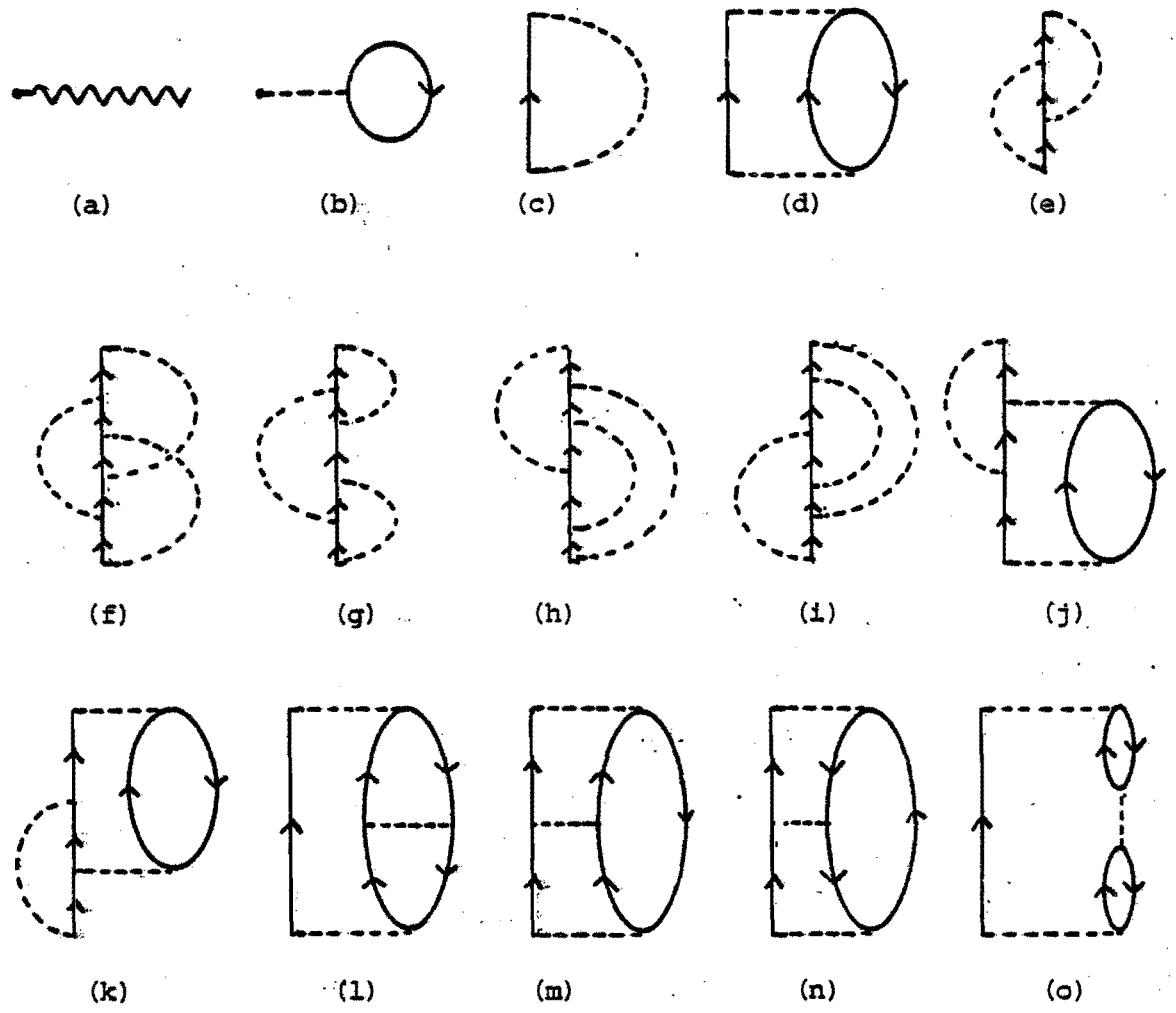


Fig.B5. All the skeleton M-structures up to the third order. (a)-(c) 1st-order structures. (d) and (e) 2nd-order structures. (f)-(o) 3rd-order structures.

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