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Self-consistent description of finite multielectron systems: new approach

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Abstract. — An analytical expression for the effective interaction in a finite multielectron system is derived. The interaction is of finite radius and is density dependent. An analytical expression is also derived for the effective single particle potential and an equation is presented for the linear response function of the considered system. Thus it is demonstrated that the spectrum, photoeffect and electron scattering cross section for such a system may be calculated by solving a complete system of integral and differential equations.

1. Introduction.

Recently an essential progress has been achieved in describing finite multielectron systems, which is connected mainly with the construction of Density Functional Theory (DFT), based on [1, 2] and with development of the Random Phase Approximation with Exchange (RPAE) [3]. This DFT in principle permits to calculate precisely the characteristics of the ground state of the system, such as the ground state energy and selfconsistent single particle effective potential. However out of its scope are those dynamic properties of the system which are closely related to the behaviour of the system in time-dependent external fields. This shortcoming of DFT was eliminated in papers [4, 5], where the Density Functional method was generalized to time-dependent densities. After this, DFT acquires the ability to consider formally static and dynamic characteristics of a finite multielectron system. However DFT is unable to derive the density functional itself. So, for its application, some approximations of this functional must be constructed [6]. Most frequently used is the Local Density Approximation (LDA), in which one has [6, 7]

$$E_{xc}[\rho] = \int \varepsilon_{xc}(\rho(r,t))\rho(r,t) \, dr.$$  \hspace{1cm} (1)

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Here $E_{xc}$ is the exchange-correlation part of the density functional, $\varepsilon_{xc}(\rho(r,t))$ is the exchange-correlation energy of the homogeneous electron gas of the density $\rho(r,t)$, related to a single particle. The exchange-correlation potential is of the form [2, 6]

$$V_{xc}(r) = \frac{\delta}{\delta \rho(r)} \left( \frac{\delta E_{xc}}{\delta \rho(r)} \right)_{\rho=\rho_0}, \tag{2}$$

with $\rho_0$ being the ground state one-particle density. The exchange-correlation effective interaction, or so-called exchange-correlation kernel [5, 6], is given by

$$R_{xc}(r; r', t') = \delta(t-t') \delta(r-r') \frac{d^2}{d\rho^2} \frac{\rho(r) \varepsilon_{xc}(\rho(r))}{\rho} |_{\rho=\rho_0}. \tag{3}$$

However, in this case the potential $V_{xc}(r)$ (2) has a wrong asymptotic behaviour at large distances $r$ from a system [6, 7], while the effective interaction $R(r; t; r', t')$ is of zero range. These limitations are quite essential, because for instance the correct asymptotic $V_{xc}(r)$ at long distances $r$ is of decisive importance for the correct description of autoionization resonances, photoionization, van der Waals forces etc. [3, 6]. The finite range dependence of the effective interaction is also essential in considering processes related to transferring considerable momentum such as the electron scattering on atoms and the photoeffect [3, 7]. We remark that in the frame of a selfconsistent description the effective interaction and the effective potential are closely linked to each other, that is an incorrect effective interaction gives rise to the incorrect effective potential. Partly this problem is solved in RPAE, where an effective potential with the correct asymptotics at large $r$ is constructed and the effective interaction is of finite range [3]. While including the inhomogeneity of the system (mainly it was applied to atoms), RPAE uses the effective interaction which completely neglects polarization phenomena, i.e. is independent of the electron density. This dependence is included in some of the generalizations of RPAE, but semiphenomenologically. To include this effect precisely, analysing and accounting for a number of sequences of the many-body theory diagrams is required which makes the problem rather complicated.

The aim of this work is the construction of a new approach to the description of finite multielectron systems. In the frame of this approach, a new equation will be derived, which determines the effective interaction $R$ and the effective one electron potential $V$, which allow to calculate static and dynamic characteristics of a finite multielectron system.

This paper is organized in the following way. In part 2 the equation for the effective interaction is derived and the means to find its solution are considered. In part 3 the effective one-electron potential is considered. Part 4 concentrates on the derivation of analytical expressions for the effective interaction and potential. Part 5 summarizes the main results of the paper.

2. Functional equation for the effective interaction.

The functional equation for the effective interaction $R$ has been derived in [8, 9]. Here we present the main points of this derivation in order to clarify the presentation of the account, and for completeness. Let us consider a system of $N$ interacting particles in its ground state. According to the prescriptions of the Density Functional Method instead of this a system of $N$ fictitious particles may be considered which are moving in an effective field $V(r)$, determined by equation [1, 2]

$$V(r) = \frac{\delta}{\delta \rho(r)} (E - T_0). \tag{4}$$
Here $T_0$ is the kinetic energy of noninteracting fictitious particles, while $E$ is the total energy of the system. We remark that $T_0$ and $E$ are functionals of the density $\rho$. In what follows we will not emphasize the difference between these particles and the fictitious ones if this will not lead to confusion.

The equation (4) may be presented as

$$V(r) = \int g v(r-r')\rho(r')\,dr' + \frac{\delta}{\delta\rho(r)} E_{xc}. \tag{5}$$

Here $g v(r-r')$ is the interparticle interaction in vacuum, $g$ is the coupling constant, while $E_{xc}$ is the exchange-correlation energy. The functional derivative in (5) is calculated at $\rho = \rho_0(r)$, where $\rho_0(r)$ is the ground state one-electron density. This condition is valid also for other functional derivatives calculated below. Instead of $E_{xc}$ the exchange-correlation part of the functional of action $A_{xc}$ can be used [4, 5], leading to the equation

$$V(r,t) = \int g v(r-r')\rho(r',t)\,dr' + \frac{\delta}{\delta\rho(r,t)} A_{xc}. \tag{6}$$

If the ground state is considered (the functional derivative is calculated at $\rho = \rho_0(r)$), the effective potential must be independent of time,

$$V(r) = \int g v(r-r')\rho(r')\,dr' + \frac{\delta}{\delta\rho(r,t)} A_{xc} \bigg|_{\rho=\rho_0} \tag{7}$$

The effective interaction $R$ is determined by the equation

$$R(r_1,t_1;r_2,t_2) = \frac{\delta}{\delta\rho(r_2,t_2)} V(r_1).$$

Of course, here $R(r_1,t_1;r_2,t_2)$ depends only upon the time difference $(t_1 - t_2) = t$:

$$R(r_1,r_2;t_1-t_2) = g v(r_1-r_2) + \frac{\delta}{\delta\rho(r_2,t)} V_{xc}(r_1). \tag{8}$$

Note, that the second term in the right part of equation (8) is equal to exchange-correlation kernel $f_{xc}$ introduced in [5]. Equations (5) and (8) are in fact only formal definitions. In order to use them one needs to express $E_{xc}$ via such functions, which permit explicit calculation of the variational derivative over density. For this reason it is convenient to use the response function apparatus. The energy $E_{xc}$ may be expressed via the linear response function and, on the other hand, there are rules on how to take variational derivatives of it over the density.

Let us use the known expression for $E_{xc}$ [10]:

$$E_{xc} = -\frac{1}{2} \int \left[ \text{Im}\chi(r_1,r_2;\omega) + \pi \rho(r_1)\delta(\omega)\delta(r_1-r_2) \right] \times g' v(r_1-r_2) \frac{dg'}{g'} \frac{d\omega}{\pi} \,dr_1 \,dr_2. \tag{9}$$

Here $\chi(r_1,r_2;\omega)$ is the linear response function and the integration over the frequency $\omega$ is performed from 0 to $+\infty$, while integration over the coupling constant goes from 0 to a real value $g$. Let us now complement equations (5, 8, 9) by an equation connecting the function $\chi(r_1,r_2;\omega)$ and the effective interaction $R(r_1,r_2;\omega)$ which is the Fourier image of the time-dependent function [5, 8, 9]:

$$R(r_1,r_2;\omega) = \chi_0^{-1}(r_1,r_2;\omega) - \chi^{-1}(r_1,r_2;\omega). \tag{10}$$
More convenient is another form:

$$
\chi(r_1, r_2; \omega) = \chi(r_1, r_2; \omega) + \int \chi_0(r_1, r_1'; \omega) R(r_1, r_2'; \omega) \chi(r_2, r_2; \omega) dr_1' dr_2'.
$$

(11)

Here \(\chi_0(r_1, r_2; \omega)\) is the linear response of fictitious Kohn-Sham particles, moving in an effective single particle field \(V(r)\). We note that exchange-correlation energy \(E_{xc}\) reduces to the exchange energy \(E_x\) if \(\chi(r_1, r_2; \omega)\) is replaced by \(\chi_0(r_1, r_2; \omega)\) in equation (9). In this case the integration over the coupling constant is trivial. The function \(\chi_0(r_1, r_2; \omega)\) is determined by the expression [11, 12]

$$
\chi_0(r_1, r_2; \omega) = \sum_i n_i [\varphi_i^*(r_1) \varphi_i(r_2) G(r_1, r_2; \varepsilon_i + \omega) + \varphi_i(r_1) \varphi_i^*(r_2) G^*(r_1, r_2; \varepsilon_i - \omega)].
$$

(12)

Here \(n_i\) is an occupation number, \(G(r_1, r_2; \omega)\) is the single particle Green's function determined by the equation

$$
G(r_1, r_2; \omega) = \sum_i \frac{\varphi_i(r_1) \varphi_i^*(r_2)}{\omega - \varepsilon_i + i\eta},
$$

(13)

where \(\varphi_i(r)\) and \(\varepsilon_i\) are the single particle Kohn-Sham wave functions and energies, respectively, \(\eta\) is an infinitesimally small positive number. These functions and energies are determined by the equation (1)

$$
\left( -\frac{\nabla^2}{2} + V(r) \right) \varphi_i(r) = \varepsilon_i \varphi_i(r).
$$

(14)

Thus equations (5, 8, 9, 11) form the system of equations which permits to calculate the functions \(R(r_1, r_2; \omega)\), \(V(r)\), \(\chi(r_1, r_2; \omega)\) and exchange-correlation energy \(E_{xc}\) of a finite many particle system, interacting with each other by the pair potential \(g v(r_1-r_2)\). For a multielectron system one has \(g v(r_1-r_2) = 1/|r_1-r_2|\). This system is considerably simplified in the case of an infinite homogeneous medium; its solution we will use as a basis to construct approximations for the effective interaction and the one-particle effective potential of a finite system. In this case the effective potential \(V(r)\) is a constant, and equation (11) may be solved analytically after performing the Fourier transformation over the space variables:

$$
\chi(q, \omega) = \frac{\chi_0(q, \omega)}{1 - R(q, \omega) \chi_0(q, \omega)}.
$$

(15)

Substituting equation (9) into equation (5) and using equation (8), we get

$$
R(r_1, r_2; t_1 - t_2) = g v(r_1 - r_2) - \frac{1}{2} \frac{\delta^2}{\delta \rho(r_1, t_1) \delta \rho(r_2, t_2)} \times \int [\text{Im} \chi(r_1', r_2'; \omega) + \pi \rho(r_1') \delta(r_1' - r_1) \delta(\omega)]

\times g' v(r_1' - r_2') \frac{dg'}{g'} \frac{d\omega}{\pi} dr_1' dr_2'.
$$

(16)

The function \(\chi(q, \omega)\), which is determined by equation (15), is conveniently presented in the following form:

$$
\chi(q, \omega) = \chi_0(q, \omega) + \frac{\chi_0^2(q, \omega) R(q, \omega)}{1 - R(q, \omega) \chi_0(q, \omega)}.
$$

(17)

(1) The atomic system of units is used in this paper.
Let us pass in equation (16) to the variables \( q \) and \( \omega \) by the Fourier transformation over space and time variables. Note, that \( R(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2) \) for a homogeneous system depends only on the coordinate difference \( |\mathbf{r}_1 - \mathbf{r}_2| \). Performing the Fourier transformation of equation (16) and using equation (17), the following equation is obtained

\[
R(q, \omega) = R_{HF}(q, \omega) - \frac{1}{2} \frac{\delta^2}{\delta \rho(q, \omega) \delta \rho(q, \omega)} \times \int \text{Im} \left[ \frac{\chi_0^2(k, \omega') R(k, \omega')}{1 - R(k, \omega') \chi_0(k, \omega')} \right] g' v(k) \frac{d \omega'}{(2\pi)^3} \frac{d \omega'}{\pi} g'.
\]

Here

\[
R_{HF}(q, \omega) = g v(q) - \frac{1}{2} \frac{\delta^2}{\delta \rho(q, \omega) \delta \rho(q, \omega)} \times \int \text{Im}[\chi_0(k, \omega')] g v(k) \frac{d \omega'}{(2\pi)^3} \frac{d \omega'}{\pi} g'.
\]

Choosing in a special way the contour of integration over the frequency \( \omega \), one can show that [10, 13] the following relation is valid

\[
\int_{0}^{\infty} \text{Im} \chi(\omega) \frac{d \omega}{\pi} = \int_{-\infty}^{\infty} \chi(i\omega) \frac{d \omega}{2\pi}
\]

With the help of equation (20), one obtains [8, 9]

\[
R(q, \omega) = R_{HF}(q, \omega) - \frac{1}{2} \frac{\delta^2}{\delta \rho(q, \omega) \delta \rho(q, \omega)} \times \int \frac{\chi_0^2(k, i\omega') R(k, i\omega')}{1 - R(k, i\omega') \chi_0(k, i\omega')} \frac{d \omega'}{(2\pi)^4} \frac{d \omega'}{\pi} g',
\]

where

\[
R_{HF}(q, \omega) = g v(q) - \frac{1}{2} \frac{\delta^2}{\delta \rho(q, \omega) \delta \rho(q, \omega)} \times \int \chi_0(k, i\omega') g v(k) \frac{d \omega'}{(2\pi)^4}.
\]

Equation (21) determines the effective interaction from which one calculates the linear response function \( \chi(q, \omega) \) of the system and the exchange-correlation energy \( E_{xc} \). Unfortunately, equations (16) and (21) are the variational equations, being in fact a compact expression of an infinite system of coupled equations [9]. In order to demonstrate this, let us clarify how to calculate the functional derivative \( \delta \chi / \delta \rho \). Such a technique will be useful later. In order to calculate this functional derivative, let us use an equation connecting the density fluctuation \( \delta \rho(\mathbf{r}, \omega) \), which appeared in the system under the action of a weak external field \( \lambda v_{ext}(\mathbf{r}, \omega) \) [12, 13]

\[
\delta \rho(\mathbf{r}, \omega) = \sum_{k=1}^{\infty} \int \frac{d \mathbf{r}_1 d \omega_1}{2\pi} \frac{d \mathbf{r}_k d \omega_k}{2\pi} \chi^{(k)}(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_k; \omega_1, \ldots, \omega_k) \times \lambda v_{ext}(\mathbf{r}_1, \omega_1) \lambda v_{ext}(\mathbf{r}_k, \omega_k) 2\pi \delta(\omega - \omega_1 - \ldots - \omega_k).
\]
Here $\chi^{(k)}$ is the causal response function of the order $k$. The equation (23) permits to determine the linear response function $\chi^{(1)} \equiv \chi(r, r_1; \omega)$ using the following equation

$$\frac{\delta \rho(r, \omega)}{\delta \lambda v_{ext}(r, \omega)} \bigg|_{\lambda=0} = \chi(r, r_1; \omega) 2\pi \delta(\omega - \omega_1). \tag{24}$$

Similarly, the response functions of higher orders may be defined. Now let us calculate the functional derivative [9]:

$$\frac{\delta \chi(r_1, r_2; \omega)}{\delta \rho(r_3, \omega)} = \frac{\int \frac{\delta \lambda v_{ext}(r_3', \omega')}{\delta \rho(r_3, \omega)} \frac{\delta^2 \rho(r_1, \omega)}{\delta \lambda v_{ext}(r_3', \omega') \delta \lambda v_{ext}(r_2, \omega)} \bigg|_{\lambda=0} \mathrm{d}r_3' \mathrm{d}\omega'}. \tag{25}$$

Taking into account equation (24), we get

$$\frac{\delta \chi(r_1, r_2; \omega)}{\delta \rho(r_3, \omega)} = 2 \int \chi^{-1}(r_3, r_3', \omega) \chi^{(2)}(r_1, r_2, r_3', \omega) \times 2\pi \delta(\omega - \omega_1 - \omega_2) \mathrm{d}r_3', \tag{26}$$

where $\chi^{(2)}$ is the second order response function and $\chi^{-1}(r, r', \omega)$ is determined by the following equation

$$\int \chi^{-1}(r, r', \omega) \chi(r', r_1, \omega) \mathrm{d}r' = \delta(r - r_1). \tag{27}$$

The calculation of the next functional derivatives is performed similarly. Thus the function $R(r_1, r_2; \omega)$ and the linear response function $\chi(r_1, r_2; \omega)$ (Eqs. (11, 21, 22)) are determined by the response functions of the second and third orders. Taking the variational derivatives of both sides of equation (21), an equation is derived which connects the response function of the second order with the response functions of the third and fourth orders etc. This procedure leads to an infinite chain of equations. This infinite chain may be transformed into a closed system of equations if an approximate relation can be established, which connects the $n$-th and $(n+1)$th response functions or an approximate expression for the variational derivative can be found. This can be done using a local approximation which works successfully for the infinite medium. In this approximation the variational derivative of the functional $F(r, \rho)$ is substituted by the following approximation:

$$\frac{\delta F(r, \rho)}{\delta \rho(r_1, t)} \approx \frac{d F(r, \rho)}{d \rho} \bigg|_{\rho=\rho_0} \delta(r - r_1) \delta(t). \tag{28}$$

Note that the approximation (28) is transformed into an equality, when integrating both sides of equation (22) over $r_1$ and $t$:

$$\int \frac{\delta F(r, \rho)}{\delta \rho(r_1, t)} \mathrm{d}r_1 \mathrm{d}t = \frac{d F(r, \rho)}{d \rho}. \tag{29}$$

Therefore, equation (28) preserves the sum rule for the compressibility of the system, which is a feature of precise solution. Let us apply the approximation (28) to transform equation (16)(or Eq. (21)) into an ordinary integro-differential equation. As a result, for the homogeneous electron fluid (or gas) the following equation is obtained [8, 9]

$$R(q, g, \rho) = R_{HF}(q, g, \rho)
- \frac{1}{2} \frac{d^2}{d \rho^2} \int \frac{\chi^2(k, i \omega) R(k, g', \rho)}{1 - R(k, g', \rho) \chi_0(k, i \omega)} \mathrm{d}k \mathrm{d} \omega \ dt g'. \tag{30}$$
Here

\[ R_{\text{HF}}(q, g, \rho) = \frac{4\pi g}{q^2} + R_{\text{F}}(q, g, \rho), \]  

(31)

where

\[ R_{\text{F}}(q, g, \rho) = -\frac{g\pi}{p_F^2} \left[ \frac{q^2}{12p_F^2} \ln \left| 1 - \frac{4p_F^2}{q^2} \right| - \frac{2p_F}{3q} \ln \left| \frac{2p_F - q}{2p_F + q} \right| + \frac{1}{3} \right]. \]  

(32)

The electron density \( \rho \) is connected to the Fermi momentum by the usual relation \( \rho = p_F^2 / 3\pi^2 \).

Having in hand the effective interaction \( R(q, g, \rho) \), one can calculate the linear response function, given by equation (15), as well as the correlation energy \( E_c \). Substituting equation (15) into equation (9) and separating the exchange energy \( E_x \), we obtain

\[ E_c = \varepsilon_c \rho = -\frac{1}{2\pi^2} \int \frac{\chi_0^2(k, \omega)R(k, g', \rho)}{1 - R(k, g', \rho)\chi_0(k, \omega)} \, dk \, d\omega \, dg'. \]  

(33)

Here \( \varepsilon_c \) is the correlation energy per electron of an electron gas of the density \( \rho \).

Based on equation (30), we will construct in the following parts of the paper approximate solutions for equations (5) and (8).

3. Asymptotic behaviour of the effective potential \( V(r) \).

In this part we will consider the asymptotic behaviour of the effective potential \( V(r) \) at \( r \to \infty \). To do this, it is convenient to separate \( V(r) \) into two terms: the exchange \( V_x(r) \) and the correlation \( V_c(r) \) [14]. Substituting equation (9) into equation (5) and separating the exchange term, we get

\[ V_x(r) = -\frac{1}{2} \frac{\delta}{\delta \rho(r, \omega)} \int \left[ \text{Im} \chi_0(r_1, r_2; \omega) + \pi \rho(r_1) \delta(\omega) \delta(r_1 - r_2) \right] \times g v(r_1 - r_2) \, dr_1 \, dr_2 \frac{d\omega}{\pi}. \]  

It is easy to demonstrate using equations (25) and (26), that the variational derivative \( \delta / \delta \rho(r, \omega) \) is transformed into a frequency independent \( \delta / \delta \rho(r) \), just as one should expect:

\[ V_x(r) = -\frac{1}{2} \frac{\delta}{\delta \rho(r)} \int \left[ \text{Im} \chi_0(r_1, r_2; \omega) + \pi \rho(r_1) \delta(\omega) \delta(r_1 - r_2) \right] \times g v(r_1 - r_2) \, dr_1 \, dr_2 \frac{d\omega}{\pi}. \]  

(34)

The correlation potential is of the form

\[ V_c(r) = -\frac{1}{2} \frac{\delta}{\delta \rho(r)} \int \left[ \chi(r_1, r_2; \omega) - \chi_0(r_1, r_2; \omega) \right] \times g' v(r_1 - r_2) \, dr_1 \, dr_2 \frac{d\omega}{\pi} \frac{dg'}{g'}. \]  

(35)

Let us calculate the potential and its asymptotics at \( r \to \infty \) using equation (26). As a result one has

\[ V_x(r) = -\frac{1}{2} \int \left[ 2\text{Im} \chi_0^{-1}(r, r') \chi_0^{(2)}(r', r_1, r_2; \omega, 0) \right] g v(r_1 - r_2) \, dr_1 \, dr_2 \frac{d\omega}{\pi}. \]  

(36)
Here $\chi_0^{(2)}(r',r_1,r_2;\omega,0)$ is the second order response function for the Kohn-Sham particles moving in the effective potential $V(r)$. The function $\chi_0^{(2)}$ is known to be analytical [12] and is determined by

$$
\chi_0^{(2)}(r',r_1,r_2;\omega_1,\omega_2) = \frac{1}{2} \sum_i n_i \{ \varphi_i^*(r') \varphi_i(r_2)G(r',r_1;\varepsilon_i + \omega_1 + \omega_2) 
\times G(r_1,r_2;\varepsilon_i + \omega_2) + \varphi_i(r') \varphi_i^*(r_2)G^*(r',r_1;\varepsilon_i - \omega_1 - \omega_2) 
\times G^*(r_1,r_2;\varepsilon_i - \omega_2) + \varphi_i(r_1) \varphi_i^*(r_2)G(r',r_1;\varepsilon_i + \omega_1) 
\times G^*(r',r_2;\varepsilon_i - \omega_2) \}.$$  \hspace{1cm} (37)

The function $\chi_0(r,r')$ is given by

$$
\chi_0(r,r') = \chi_0(r,r';\omega)|_{\omega=0},
$$

and $\chi_0^{-1}(r,r')$ is given by

$$
\int \chi_0^{-1}(r,r') \chi_0(r',r_1) \, dr' = \delta(r-r_1). \hspace{1cm} (38)
$$

After integration over frequency $\omega$ and some algebra, equation (36) is transformed into [15]

$$
V_x(r) = -\int \chi_0^{-1}(r,r') \sum_{ii} n_i n_i \{ \varphi_i^*(r_2) \varphi_i(r_1) \varphi_i(r') \varphi_i^*(r_1) 
\times G(r_2,r',\varepsilon_i) + \varphi_i(r_2) \varphi_i^*(r_1) \varphi_i(r') \varphi_i(r_1) 
\times G^*(r_2,r';\varepsilon_i) \} \, g(v(r_1 - r_2)) \, dr_1 \, dr_2 \, dr'. \hspace{1cm} (39)
$$

Equation (39) determines the exact exchange potential of Density Functional Theory. Note that the potential $V_x(r)$ for $g(v(r_1 - r_2) = 1/(r_1 - r_2)$ coincides with the known Talman-Shadwick potential [16], which was derived in the Hartree-Fock approximation for the ground state energy. So we resume that equation (39) is the generalization of this potential.

In order to calculate $V_x(r)$ at $r \rightarrow \infty$ let us use the equation (39) and assume, that if $r \rightarrow \infty$ then $r_2 \rightarrow \infty$ also. Using the fact, that $r_2 \gg r_1$ and performing the integration over $r_1$, we obtain

$$
V_x(r)|_{r \rightarrow \infty} = -\int \chi_0^{-1}(r,r') \sum_i n_i \{ \varphi_i^*(r_2) \varphi_i(r') G(r_2,r',\varepsilon_i) 
\times \varphi_i(r_2) \varphi_i(r') G^*(r_2,r',\varepsilon_i) \} \, g(v(r_2)) \, dr' 
\times G^*(r_2,r';\varepsilon_i) \} \, g(v(r_2)) \, dr_2 \, dr'. \hspace{1cm} (40)
$$

Note, that $g(v(r_1 - r_2) = g(v(r_2)$ as $r_2 \rightarrow \infty$. Using equation (38), we get

$$
V_x(r) = -\int \delta(r-r_2) \, g(v(r_2)) \, dr_2 = -g(v(r). \hspace{1cm} (41)
$$

In the case, when $g(v(r) = 1/r$, one has the known result:

$$
V(r)|_{r \rightarrow \infty} = -\frac{1}{r}.
$$
Note that the equation (41) confirms our assumption that \( r_2 \to \infty \) when \( r \to \infty \). Unfortunately, it is impossible to obtain an analytical expression for \( V_c(r) \), because this requires knowledge of the precise linear response function \( \chi \), or effective interaction \( R \). However the asymptotic expression at large \( r \) is known [17]

\[
V_c(r)|_{r \to \infty} = -\frac{\alpha^2}{2r^4},
\]

where \( \alpha \) is the static polarizability.

4. The system of equations for description of a finite multielectron system.

In order to describe a finite multielectron system, such as an atom or a metallic cluster, the equations (9, 11, 16, 35, 39) must be solved. As a result one can obtain the ground state energy, the effective potential, the effective interaction and the linear response function. Having the linear response function, it is possible to calculate the probabilities and cross sections of different processes taking place with the system in an external field, just as the characteristics of the system. Thus, having the response function, one can calculate the inelastic electron scattering cross section upon an atom. In what follows by "atom" we mean any finite multielectron system, such as, e.g., a metallic cluster or an atom itself.

The inelastic scattering cross section in the Distorted Wave Born Approximation is given by [18]

\[
\frac{d\sigma(\omega, q)}{d\omega dq} = \frac{1}{\pi} \text{Im} \int e^{iq(r_1-r_2)}\chi(r_1, r_2; \omega) \, dr_1 \, dr_2 \frac{d\sigma^{el}(q)}{dq}.
\]

Here \( q \) and \( \omega \) are transferred momentum and energy loss, while \( d\sigma^{el}/dq \) is the elastic electron-electron scattering cross section. Similarly the interaction of an atom with radiation, i.e. with monochromatic spatially constant electric field in \( z \)-direction with a frequency \( \omega \), can be considered [3, 7]. For instance, the photoabsorption cross section is given by [7]

\[
\sigma(\omega) = -4\pi \omega \text{Im} \int z'z' \chi(r, r'; \omega) \, dr \, dr'.
\]

The linear response function \( \chi(r_1, r_2; \omega) \) has the following spectral representation [10]:

\[
\chi(r_1, r_2; \omega) = \sum_{n \neq 0} \left[ \frac{(0|\hat{\rho}(r_1)|n)(n|\hat{\rho}(r_2)|0)}{\omega - (E_n - E_0) + i\eta} - \frac{(0|\hat{\rho}(r_2)|n)(n|\hat{\rho}(r_1)|0)}{\omega + (E_n - E_0) + i\eta} \right].
\]

Here \( \hat{\rho}(r) \) is the electron density operator, \( |0> \) and \( |n> \) are the many-particle system's exact ground and excited states respectively. \( E_0 \) and \( E_n \) are energies of these states. It is seen from (45) that the poles of \( \chi(r_1, r_2; \omega) \) as a function of \( \omega \) determine the spectrum of the system, while the residues determine the probabilities of the transitions from \( <0| \) to \( |n> \) states. So, we see that the response function includes vast information upon the described system.

Let us now construct the response function \( \chi \). This function may be obtained by solving the equations (9, 11, 16, 35, 39).

This is a system of functional equations, the solution of which is connected with big difficulties of both mathematical and computing character. Therefore, let us use equation (30) in order to calculate approximations for the effective interaction \( R(r_1, r_2; \omega) \), the effective potential \( V(r) \) and the response function \( \chi(r_1, r_2; \omega) \). Equation (30) determines frequency independent effective interaction in an infinite homogeneous multielectron system (jellium model). Then, having at hand function \( R(q, \rho) \), one can in the local density approximation construct the
Table I. — Correlation energy per electron in eV of an electron gas of density \( r_s \). The Monte Carlo results \([19]\) \( \varepsilon_c^M \) are compared with the calculations of \([8]\). \( \varepsilon_c \) denotes the results of exact calculations, and \( \varepsilon_c^I \) denotes the results of the calculations when the effective interaction \( R \) was approximated by \( R_{HF} \).

<table>
<thead>
<tr>
<th>( r_s )</th>
<th>( \varepsilon_c^M )</th>
<th>( \varepsilon_c )</th>
<th>( \varepsilon_c^I )</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>-1.62</td>
<td>-1.62</td>
<td>-1.62</td>
</tr>
<tr>
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<td>-1.01</td>
<td>-1.02</td>
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</tr>
<tr>
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<td>-0.56</td>
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<td>-0.38</td>
</tr>
<tr>
<td>50</td>
<td>-0.16</td>
<td>-0.17</td>
<td>-0.22</td>
</tr>
</tbody>
</table>

effective interaction \( R(r_1, r_2) \) in a finite system. The local density approximation proves to be rather successful even in atomic systems, where the density varies rather fast and therefore one can expect, that in more homogeneous systems, like metallic clusters, this approximation will work even better. On the other hand, it appears that the dependence of the effective interaction upon the frequency is inessential while describing such processes as photoionization or photoabsorption, where its contribution is estimated as being less than 1 % \([5]\). Thus, one may expect that the function \( R(q, \rho) \) is quite suitable for constructing the effective interaction in a finite system. Then, knowing the effective interaction \( R(r_1, r_2) \), one can next use the local density approximation and construct the effective single particle potential \( V(r) \), which permits to solve the single particle Schrödinger equation (14) in a self-consistent way. As a result, after calculating the Kohn-Sham orbitals \( \varphi_i \) and energies \( \varepsilon_i \), one can construct the response function \( \chi_0(r_1, r_2; \omega) \) (Eq. (12)) and the linear response function \( \chi(r_1, r_2; \omega) \) (Eq. (11)) which may be used to consider different processes discussed above. So, in accordance with the described program, let us start with the construction of \( R(r_1, r_2) \).

As can be seen from table I, the effective interaction \( R(q, \rho) \), being the solution of equation (30), permits to describe the electron gas correlation energy \( \varepsilon_c \) (see Eq.(33)) in a rather broad interval of density variation. Note, that at \( r_s = 50 \) the mistake is no more than 5 % as compared to Monte Carlo calculations, at \( r_s = 30 \) the mistake is 1 %, while at \( r_s \to 0 \) the results, quite naturally are in agreement with the Random Phase Approximation. Here \( r_s = (3/4\pi \rho)^{1/3} \). So, one can use the numerical solution of equation (30) to construct the function \( R(r_1, r_2) \).

However, it is more convenient to employ the analytical approximation \( R_{HF}(q, \rho) \) given by equation (31). Note, that the one-electron density of a metallic cluster is nearly equal to that of a metal. It is seen from table I that \( R_{HF} \) gives a very good description of the correlation energy at metallic densities. The result becomes exact when \( r_s \to 0 \) \([8]\). So we conclude that one can use the function \( R_{HF} \) as the effective interaction between electrons in an infinite system. None the less we can correct this approximation in a rather simple way. The solution of equation (30) may be written as

\[
R(q, \rho) = \frac{4\pi}{q^2} + R_F(q, \rho) + R_c(q, \rho). \tag{46}
\]
It follows straightforwardly from equations (31), (32) that

\[ R_F(q, \rho)|_{q=0} = \frac{d^2}{d\rho^2} (\varepsilon_x \rho), \]  

(47)

with \( \varepsilon_x \) being the exchange energy per electron, while

\[ R_c(q, \rho)|_{q=0} = \frac{d^2}{d\rho^2} (\varepsilon_c \rho), \]  

(48)

as it follows from equations (30), (33) and (46), where \( \varepsilon_c \) is correlation energy per electron. The function \( R_c(q, \rho) \) is calculated numerically, and as a result the ratio \( \Delta(q) = R_c(q, \rho)/R_F(q, \rho) \) may be estimated [9] (see Eqs. (46, 47))

\[ \Delta(q)|_{q=0} = \frac{\frac{d^2}{d\rho^2} (\varepsilon_c \rho)}{\frac{d^2}{d\rho^2} (\varepsilon_x \rho)} \approx \frac{\varepsilon(r_s) r_s}{2}, \]  

(49)

where \( \varepsilon_c(r_s) \) is the correlation energy per electron of the electron gas with density \( r_s \), measured in atomic units. Using table I, it is easy to demonstrate that for \( r_s = 1 \) one has \( \Delta \approx 0.05 \) for \( r_s = 10 \) it is \( \Delta \approx 0.15 \) and even for \( r_s = 50 \) the quantity \( \Delta \) becomes equal to \( \Delta \approx 0.25 \). So, for reasonable electron densities the correction \( R_c(q, \rho) \) is comparatively small, and \( R_c(q, \rho) \) may be accounted for using the simple approximation

\[ R(q, \rho) = \frac{4\pi}{q^2} + R_F(q, \rho) [1 + \Delta(q)|_{q=0}]. \]  

(50)

Equation (50) preserves equation (49) and reproduces the \( R_c(q, \rho) \) dependence upon \( q \) reasonably well for the electron densities of interest [21]. Of course, one may use a more sophisticated approximation [9] for \( R_c(q, \rho) \), but we should bear in mind that this function is a comparatively small correction.

Now let us use equation (50) to construct the effective interaction for a finite inhomogeneous system in the local density approximation. It means, that we shall assume that the effective interaction in a finite system at a point \( r_1 \) with the one-electron density \( \rho(r_1) \) is the same as in an infinite homogeneous medium with the density \( \rho = \rho(r_1) \).

In coordinate representation the effective interaction \( R(r_1, r_2) \) may be derived using the Fourier transformation

\[ R(r_1, r_2) = \int R(q, \rho) e^{i\mathbf{q}(r_1 - r_2)} \frac{d\mathbf{q}}{(2\pi)^3}. \]  

(51)

After straightforward calculations one obtains

\[ R(r_1, r_2) = v(r_1 - r_2) \left\{ 1 + \frac{1}{2x^2} \left[ 1 - \frac{p_F^2}{\pi} \left( \frac{r_1 + r_2}{2} \right) \right] \right\} \times \frac{d^2}{d\rho^2} \left[ \rho \left( \frac{r_1 + r_2}{2} \right) \varepsilon_c \left( \rho \left( \frac{r_1 + r_2}{2} \right) \right) \right] \left[ \cos 2x - \frac{\sin 2x}{x} + \frac{\sin^2 x}{x^2} \right]. \]  

(52)

Here \( v(r_1 - r_2) = 1/|r_1 - r_2| \), and

\[ x = \left| r_1 p_F(r_1) - r_2 p_F(r_2) \right|. \]  

(53)

The function \( p_F(r) \) is related to the single-electron density

\[ p_F(r) = [3\pi^2 \rho(r)]^{1/3}. \]  

(54)
We remark that the effective interaction (52) depends symmetrically on the spatial coordinates

$$R(r_1, r_2) = R(r_2, r_1).$$

(55)

Using equation (11) and equation (55) one can obtain

$$\chi(r_1, r_2; \omega) = \chi(r_2, r_1; \omega),$$

(56)

as it should be.

To calculate the effective single-particle potential $V(r)$ let us use equation (8). Bearing in mind that the effective interaction $R(r_1, r_2)$ does not depend on the frequency $\omega$, we obtain [5, 8, 22]

$$R(r_1, r_2) = \frac{\delta}{\delta \rho(r_2)} V(r_1).$$

(57)

To solve equation (57) let us use the local density approximation and act just as when calculating the effective interaction $R(r_1, r_2)$ of a finite system. The contribution to $V(r)$ related with the correlation $R_c(q, \rho)$ (see Eq. (46)) we shall take into account in the simplest way

$$V_c(r) = \frac{\partial}{\partial \rho} [\varepsilon_c(\rho(r)) \rho(r)].$$

(58)

Such procedure enables us to derive $V(r)$ in an analytical form. After performing straightforward calculations one has:

$$V(r_1) = \int v(r_1 - r_2) \rho(r_2) \left[ 1 + \frac{3}{2x^3} \left( \frac{\sin 2x}{2} - \frac{\sin^2 x}{x} \right) \right] \, dr_2$$

$$+ \frac{\partial}{\partial \rho} [\varepsilon_c(\rho(r_1)) \rho(r_1)]$$

$$+ 3 \int v(r_1 - r_2) \rho_0(r_2) \frac{1}{x_1^3} \left( \frac{\sin 2x_1}{2} - \frac{\sin^2 x_1}{x_1} \right) \, dr_2.$$

(59)

Here $x$ is given by (53), $x_1 = |r_1 - r_2|/p_F(r_1)$, and $\rho_0(r)$ is the single-electron density, normalized so that $\int \rho_0(r) \, dr = 1$. The third term in equation (59) vanishes in the case of an infinite medium and provides the correct asymptotic behaviour of the effective potential (see Eq. (40))

$$V(r)|_{r \to \infty} = - \frac{1}{r}$$

(60)

Taking the results of section 3 as a basis and using equations (26, 34, 35), one can express $V(r)$ in terms of the response functions of the first and the second order, as was done when calculating the exchange potential $V_x(r)$

$$V(r) = - \frac{1}{2} \int [2 \text{Im} \chi^{-1}(r, r') \chi(2)(r', r_1, r_2; \omega)$$

$$+ \pi \delta(r_1 - r_2) \delta(r - r_1) \delta(\omega)] \frac{1}{|r_1 - r_2|} \, dr_1 \, dr_2 \, d\omega.$$

(61)

Equation (61) ensures the correct asymptotics of $V(r)$ at large $r$, but from a numerical point of view it is very difficult to use equation (61) to calculate $V(r)$. 
Now let us briefly consider a pair correlation function \( g(r_1, r_2) \). \( g(r_1, r_2) \) is related to the linear response function [10]

\[
\rho(r_1)\rho(r_2)[g(r_1, r_2) - 1] = -\int \text{Im} \chi(r_1, r_2; \omega) \frac{d\omega}{\pi} - \rho(r_1)\delta(r_1 - r_2). \tag{62}
\]

As follows from equations (62) and (56),

\[
g(r_1, r_2) = g(r_2, r_1). \tag{63}
\]

With help of equation (62) we may conclude that the well-known sum rule is satisfied

\[
\int \rho(r_1)[g(r_1, r_2) - 1] dr_1 = -1. \tag{64}
\]

The relation (64) immediately follows from equation (62) if we make use of the relation [12]

\[
\int \chi(r_1, r_2; \omega) dr_2 = 0. \tag{65}
\]

The exchange-correlation energy \( E_{xc} \), as follows from equations (9) and (62), is given by

\[
E_{xc} = \frac{1}{2} \int [g(r_1, r_2) - 1] \rho(r_1)\rho(r_2)g'(r_1 - r_2) \frac{dg'}{g'} dr_1 dr_2. \tag{66}
\]

So we may conclude that in our approach the function \( g(r_1, r_2) \) is defined in a selfconsistent manner, while the well known relations (63, 64, 66) are satisfied.

In this section we have derived the equations for description of a finite electron system. Having in mind the description of a many-electron finite system we have to simplify our equations as much as possible. This problem is resolved. Indeed, the effective potential is given by equation (59). Using the single-particle equation (14), we calculate the one-particle Kohn-Sham orbitals \( \varphi_i(r) \), the energies \( \varepsilon_i \) and the single electron density

\[
\rho(r) = \sum n_i \varphi_i^*(r) \varphi_i(r).
\]

The linear Kohn-Sham response function \( \chi_0(r_1, r_2; \omega) \) is given by equation (12), while the effective interaction \( R(r_1, r_2) \) is defined by equation (52). Having in hand the functions \( \chi_0 \) and \( R \) and using equation (11) one can calculate the linear response function \( \chi(r_1, r_2; \omega) \). Using \( \chi(r_1, r_2; \omega) \), as was shown above, the characteristics of different processes may be calculated.

5. Summary and discussion.

Let us now discuss the main results. We have suggested a new approach to calculate the effective interaction \( R(r_1, r_2) \), the effective single particle potential \( V(r) \) and the linear response function \( \chi(r_1, r_2; \omega) \) of a finite inhomogeneous many-electron system. Our approach is free from any adjustable parameters, the function \( R(r_1, r_2) \) has a finite range coordinate dependence, correspondingly the function \( V(r) \) has the asymptotic form \( V(r)|_{r \to \infty} = -1/r \). Having in hand the function \( \chi(r_1, r_2; \omega) \) one can calculate the spectrum of the many-electron system, the characteristics of its interaction with electromagnetic radiation and the electron scattering upon the system.
Now we shall briefly compare the equations obtained here with equations of the approach grounded on Time Dependent Local Density Approximation (TDLDA) [5, 7, 22] and with the well-known RPAE [3]. In TDLDA the effective interaction has a δ-type coordinate dependence, while the effective potential falls off exponentially at largest r. The finite range dependence of the effective interaction and the asymptotic behaviour of the effective potential are of crucial importance in studying negative ions and autoionization resonances, as well as a photoabsorption and a photoeffect cross section in the vicinity of its threshold. Also these features are essential in considering processes connected with transferring considerable momentum, for instance, in electron scattering on atoms and in the photoeffect [3, 7, 22]. The equations derived by us may be reduced to those of TDLDA if we use a δ-type coordinate dependent effective interaction instead of the finite range effective interaction.

In RPAE, which is based on the Hartree-Fock approximation for the ground state, the effective interaction is taken as a sum of the bare Coulomb interaction and the exchange one, so the correlation contribution to the effective interaction and the effective potential is almost completely neglected [3]. Note that this contribution is of great importance at a comparatively low density as it is, for instance, in a metallic cluster. The RPAE equations may be obtained from the derived equations if the exchange-correlation part of the effective interaction is substituted by the exchange Coulomb interaction.

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