NEW APPROACH TO DENSITY FUNCTIONAL THEORY AND DESCRIPTION OF SPECTRA OF FINITE ELECTRON SYSTEMS

M.Ya. Amusia\textsuperscript{a,b}, A.Z. Msezane\textsuperscript{c}, and V.R. Shaginyan\textsuperscript{c,d} *
\textsuperscript{a} The Racah Institute of Physics, the Hebrew University, Jerusalem 91904, Israel;
\textsuperscript{b} Physical-Technical Institute, 194021 St. Petersburg, Russia;
\textsuperscript{c} CTSPS, Clark Atlanta University, Atlanta, Georgia 30314, USA;
\textsuperscript{d} Petersburg Nuclear Physics Institute, Gatchina, 188300, Russia

Abstract

The self consistent version of the density functional theory is presented, which allows to calculate the ground state and dynamic properties of finite multi-electron systems. An exact functional equation for the effective interaction, from which one can construct the action functional, density functional, the response functions, and excitation spectra of the considered systems, is outlined. In the context of the density functional theory we consider the single particle excitation spectra of electron systems and relate the single particle spectrum to the eigenvalues of the corresponding Kohn-Sham equations. We find that the single particle spectrum coincides neither with the eigenvalues of the Kohn-Sham equations nor with those of the Hartree-Fock equations.

\textit{PACS:} 31.15.Ew; 31.50.+w

*E-mail: vrshag@thd.pnpi.spb.ru
I. INTRODUCTION

The density functional theory (DFT), that originated from the pioneering work of Hohenberg and Kohn [1], has been extremely effective in describing the ground state of finite many-electron systems. Such a success gave birth to many papers concerned with the generalization of DFT, which would permit the description of the excitation spectra also. The generalization, on theoretical grounds, originated mainly from the Runge-Gross theorem, which helped to transform DFT into the time-dependent density functional theory TDDFT [3]. Both, DFT and TDDFT, are based on the one-to-one correspondence between particle densities of the considered systems and external potentials acting upon these particles. Unfortunately, the one-to-one correspondence establishes only the existence of the functionals in principle, leaving aside a very important question on how one can construct them in reality. This is why the successes of DFT and TDDFT strongly depend upon the availability of good approximations for the functionals. This shortcoming was resolved to a large extent in [2,4,5] where exact equations connecting the action functional, effective interaction and linear response function were derived. But the linear response function, containing information of the particle-hole and collective excitations, does not directly present information about the single particle spectrum.

In this Report, the self consistent version of the density functional theory is outlined, which allows to calculate the ground state and dynamic properties of finite multi-electron systems starting with the Coulomb interaction. An exact functional equation for the effective interaction, from which one can construct the action functional, density functional, the response functions, and excitation spectra of the considered systems, is presented. The effective interaction relating the linear response function of non-interacting particles to the exact linear response function is of finite radius and density dependent. We derive equations describing single particle excitations of multi-electron systems, using as a basis the exact functional equations, and show that single particle spectra do not coincide either with the eigenvalues of the Kohn-Sham equations or with those of the Hartree-Fock equations.

II. EXACT EQUATION FOR THE FUNCTIONAL

Let us briefly outline the equations for the exchange-correlation functional $E_{xc}[\rho]$ of the ground state energy and exchange-correlation functional $A_{xc}[\rho]$ of the action $A[\rho]$ in the case when the system in question is not perturbed by an external field. In that case an equality holds [2,4]

$$E_{xc}[\rho] = A_{xc}[\rho]|_{\rho(r, \omega=0)},$$

since $A_{xc}$ is also defined in the static densities domain. The exchange-correlation functional $E_{xc}[\rho]$ is defined by the total energy functional $E[\rho]$ as

$$E[\rho] = T_k[\rho] + \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 + E_{xc}[\rho],$$

where $T_k[\rho]$ is the functional of the kinetic energy of the non-interacting Kohn-Sham particles. The atomic system of units $e = m = \hbar = 1$ is used in this paper. The exchange-correlation functional may be obtained from [2]
\[ E_{xc}[\rho] = -\frac{1}{4\pi} \int \left[ \chi(r_1, r_2, iw, g') + 2\pi \rho(r_1)\delta(w)\delta(r_1 - r_2) \right] \frac{dwdgdr_1dr_2}{|r_1 - r_2|}. \] (3)

Equation (3) represents the expression for the exchange-correlation energy of a system [2], expressed via the linear response function \( \chi(r_1, r_2, iw, g') \), with \( g' \) being the coupling constant. For Eq. (3) to describe \( A_{xc}[\rho] \) and \( E_{xc}[\rho] \) the only thing we need is the ability to calculate the functional derivatives of \( E_{xc}[\rho] \) with respect to the density. According to Eq. (3), it means an ability to calculate the functional derivatives of the linear response function \( \chi \) with respect to the density \( \rho(r, \omega) \) which was developed in [2,5,6]. The linear response function is given by the integral equation

\[ \chi(r_1, r_2, \omega) = \chi_0(r_1, r_2, \omega) + \int \chi_0(r_1, r'_1, \omega)R(r'_1, r'_2, \omega)\chi(r'_2, r_2, \omega)dr'_1dr'_2, \] (4)

with \( \chi_0 \) being the linear response function of non-interacting particles, moving in the single particle time-independent field [2,5]. It is evident that the linear response function \( \chi(g) \) tends to the linear response function of the system in question as \( g \) goes to 1. The exact functional equation for \( R(r_1, r_2, \omega, g) \) is [2,5]

\[ R(r_1, r_2, \omega, g) = \frac{g}{|r_1 - r_2|} \]

\[-\frac{1}{2} \frac{\delta^2}{\delta \rho(r_1, \omega)} \frac{\delta^2}{\delta \rho(r_2, -\omega)} \int_0^g \chi(r'_1, r'_2, iw, g') \frac{1}{|r'_1 - r'_2|} dr'_1dr'_2 \frac{dw}{2\pi} dg'.\] (5)

Here \( R(r_1, r_2, \omega, g) \) is the effective interaction depending on the coupling constant \( g \) of the Coulomb interaction. The coupling constant \( g \) in Eq. (5) is in the range \((0 - 1)\). The single particle potential \( v_{xc} \), being time-independent, is determined by the relation [2,5],

\[ v_{xc}(r) = \frac{\delta}{\delta \rho(r)} E_{xc}[\rho]. \] (6)

Here the functional derivative is calculated at \( \rho = \rho_0 \) with \( \rho_0 \) being the equilibrium density. By substituting (3) into (6), it can be shown that the single particle potential \( v_{xc} \) has the proper asymptotic behavior [5,6],

\[ v_{xc}(r \rightarrow \infty) \rightarrow v_x(r \rightarrow \infty) \rightarrow -\frac{1}{r}. \] (7)

The potential \( v_{xc} \) determines the energies \( \varepsilon_i \) and the wave functions \( \phi_i \)

\[ \left( -\frac{\nabla^2}{2} + V_H(r) + V_{ext}(r) + v_{xc}(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r). \] (8)

These constitute the linear response function \( \chi_0(r_1, r_2, \omega) \) entering Eq. (4)

\[ \chi_0 = \sum_{i,k} n_i(1 - n_k)\phi_i^*(r_1)\phi_i(r_2)\phi_k^*(r_2)\phi_k(r_1) \left[ \frac{1}{\omega - \omega_{ik} + i\eta} - \frac{1}{\omega + \omega_{ik} - i\eta} \right] \] (9)

and the real density of the system \( \rho \),
\[ \rho(r) = \sum_i n_i |\phi_i(r)|^2. \]  

(10)

Here \( n_i \) are the occupation numbers, \( V_{\text{ext}} \) contains all external single particle potentials of the system, viz. the Coulomb potentials of the nuclei. \( E_H \) is the Hartree energy

\[ E_H = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2, \]

(11)

with the Hartree potential \( V_H(r) = \delta E_H / \delta \rho(r) \), and \( \omega_{ik} \) is the one-particle excitation energy \( \omega_{ik} = \varepsilon_k - \varepsilon_i \), and \( \eta \) is an infinitesimally small positive number.

### III. THE EFFECTIVE INTERACTION

The above equations (2-5) solve the problem of calculating \( E_{xc} \), the ground state energy and the particle-hole and collective excitation spectra of a system without resorting to approximations for \( E_{xc} \), based on additional and foreign inputs to the considered problem, such as found in calculations such as Monte Carlo simulations. We note, that using these approximations, one faces difficulties in constructing the effective interaction of finite radius and the linear response functions [1]. On the basis of the suggested approach, one can solve these problems. For instance, in the case of a homogeneous electron liquid it is possible to determine analytically an efficient approximate expression \( R_{\text{RPAE}} \) for the effective interaction \( R \), which essentially improves the well-known Random Phase Approximation by taking into account the exchange interaction of the electrons properly, thus forming the Random Phase Approximation with Exchange [4,5]. The corresponding expression for \( R_{\text{RPAE}} \) is

\[ R_{\text{RPAE}}(q, g, \rho) = \frac{4\pi g}{q^2} + \frac{\delta E_x}{\delta \rho} = \frac{4\pi g}{q^2} + R_E(q, g, \rho), \]

(12)

where

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

(13)

Here \( E_x \) is the exchange energy given by Eq. (3) when \( \chi \) is replaced by \( \chi_0 \). The electron density \( \rho \) is connected to the Fermi momentum by the ordinary relation \( \rho = p_F^3 / 3\pi^2 \). Having in hand the effective interaction in \( R_{\text{RPAE}} \), one can calculate the correlation energy \( \varepsilon_c \) per electron of an electron gas with the density \( r_s \). The dimensionless parameter \( r_s = r_0 / a_B \) is usually introduced to characterize the density, with \( r_0 \) being the average distance between electrons, and \( a_B \) is the Bohr radius.

| \( r_s \) | \( \varepsilon_c^M \) | \( \varepsilon_c^{\text{RPA}} \) | \( \varepsilon_c^{\text{RPAE}} \) |
|---|---|---|---|
| 1 | -1.62 | -2.14 | -1.62 |
| 3 | -1.01 | -1.44 | -1.02 |
| 5 | -0.77 | -1.16 | -0.80 |
| 10 | -0.51 | -0.84 | -0.56 |
| 20 | -0.31 | -0.58 | -0.38 |
| 50 | -0.16 | -0.35 | -0.22 |
In the Table, Monte Carlo results \( \varepsilon^c_M \) are compared with the results of the RPA calculation \( \varepsilon^c_{RPA} \), and \( \varepsilon^c_{RPAE} \) when the effective interaction \( R \) was approximated by \( R_{RPAE} \) [2,4]. The energies per electron are given in eV. Note that the effective interaction \( R_{RPAE}(q, \rho) \) permits the description of the electron gas correlation energy \( \varepsilon^c \) in an extremely broad range of the variation of the density. At \( r_s = 10 \) the error is no more than 10% of the Monte Carlo calculations, while the result becomes almost exact at \( r_s = 1 \) and is exact when \( r_s \to 0 \) [2,4].

**IV. SINGLE-PARTICLE SPECTRUM**

Now let us calculate the single particle energies \( \epsilon_i \), that, generally speaking, do not coincide with the eigenvalues \( \epsilon_i \) of Eq. (8). Note that these eigenvalues \( \epsilon_i \) do not have a physical meaning and cannot be regarded as the single-particle energies (see e.g. [1]). To calculate the single particle energies one can use the Landau equation [8]

\[
\frac{\delta E}{\delta n_i} = \epsilon_i. \tag{14}
\]

In order to illustrate how to calculate the single-particle energies \( \epsilon_i \) within the DFT, we choose the simplest case when the functional \( E_{xc} \) is approximated by \( E_x \). As we shall see, the single-particle energies \( \epsilon_i \) coincide neither with the eigenvalues calculated within the Hartree-Fock (HF) method nor with \( \epsilon_i \) of Eq. (8). To proceed, we use a method developed in [5]. The linear response function \( \chi_0 \) and density \( \rho(r) \), given by Eqs. (9) and (10) respectively, depend upon the occupation numbers. Thus, one can consider the ground state energy \( E \) as a functional of the density and the occupation numbers

\[
E[\rho(r), n_i] = T_k[\rho(r), n_i] + E_H[\rho(r), n_i] + E_x[\rho(r), n_i] + \int V_{ext}(r)\rho(r)dr. \tag{15}
\]

Here \( T_k \) is the functional of the kinetic energy of noninteracting particles. As it follows from Eq. (3), the functional \( E_x \) is given by [6]

\[
E_x[\rho] = -\frac{1}{4\pi} \int [\chi_0(r_1, r_2, iw) + 2\pi \rho(r_1)\delta(w)\delta(r_1 - r_2)] \frac{dwdr_1dr_2}{|r_1 - r_2|}. \tag{16}
\]

Upon using Eq. (16), the exact exchange potential \( v_x(r) = \delta E_x/\delta\rho(r) \) of DFT can be calculated explicitly [6]. Substituting Eq. (15) into Eq. (14) and remembering that the single-particle wave functions \( \phi_i \) and eigenvalues \( \epsilon_i \) are given by Eq. (8) with \( v_{xc}(r) = v_x(r) \), we see that the single particle spectrum \( \epsilon_i \) can be represented by the expression

\[
\epsilon_i = \epsilon_i - < \phi_i | v_x | \phi_i > + \frac{\delta E_x}{\delta n_i}. \tag{17}
\]

The first and second terms on the right hand side in Eq. (17) are determined by the derivative of the functional \( T_k \) with respect to the occupation numbers \( n_i \). To calculate the derivative we consider an auxiliary system of non-interacting particles in a field \( U(r) \). The ground state energy \( E_0^U \) of this system is given by the following equation

\[
E_0^U = T_k + \int U(r)\rho(r)dr. \tag{18}
\]
Varying $E_0^U$ with respect to the occupation numbers, one gets the desired result

$$
\varepsilon_i = \frac{\delta E_0^U}{\delta n_i} = \frac{\delta T_k}{\delta n_i} + \langle \phi_i | U | \phi_i \rangle,
$$

(19)

provided $U = V_H + v_x + V_{ext}$. The third term on the right hand side of Eq. (17) is related to the contribution coming from $E_x$ defined by Eq. (16). In the considered simplest case when we approximate the functional $E_{xc}$ by $E_x$, the coupling constant $g$ enters $E_x$ as a linear factor. If we omit the inter-electron interaction, $g \to 0$, that is, we put $E_x \to 0$, we directly get from Eq. (17) $\varepsilon_i = \varepsilon_i$ as it must be in the case of a noninteracting system of electrons. Note that it is not difficult to include the correlation energy in the simplest local density approximation

$$
E_c[\rho, n_i] = \int \rho(r) \varepsilon_c(\rho(r)) dr.
$$

(20)

Here the density $\rho(r)$ is given by Eq. (10) and the correlation potential is defined as

$$
V_c(r) = \frac{\delta E_c[\rho]}{\delta \rho(r)}.
$$

(21)

Varying $E[\rho(r), n_i]$ with respect to the occupation numbers $n_i$ and after some straightforward calculations, we obtain the rather simple expression for the single particle spectrum

$$
\varepsilon_i = \varepsilon_i - \langle \phi_i | v_x | \phi_i \rangle - \sum_k n_k \int \frac{\phi_i^*(r_1) \phi_i^*(r_2) \phi_k^*(r_1) \phi_k(r_2)}{r_1 - r_2} dr_1 dr_2.
$$

(22)

Here $\varepsilon_i$ are the eigenvalues of Eq. (8) with $v_{xc} = v_x + V_c$. We employ Eq. (19) and choose the potential $U$ as $U = V_H + v_x + V_c + V_{ext}$ to calculate the derivative $\delta T_k/\delta n_i$. Approximating the correlation functional $E_c[\rho, n_i]$ by Eq. (20), we simplify the calculations a lot, preserving at the same time the asymptotic condition, $(v_x + V_c)_{r \to \infty} \to -1/r$. This condition is of crucial importance when calculating the wave functions and eigenvalues of vacant states within the framework of the DFT approach [5]. Note, that these functions and eigenvalues that enter Eq. (22) determine the single particle spectrum $\varepsilon_i$. This spectrum has to be compared with the experimental results. The single particle levels $\epsilon_i$, given by Eq. (22), resemble the eigenvalues $\varepsilon_i^{HF}$ that are obtained within the HF approximation. If the wave functions $\phi_i$ would be solutions of the HF equations and the correlation potential $V_c(r)$ would be omitted, the energies $\epsilon_i$ would exactly coincide with the HF eigenvalues $\varepsilon_i^{HF}$. But this is not the case, since $\phi_i$ are solutions of Eq. (8), and the energies $\epsilon_i$ do not coincide with either $\varepsilon_i^{HF}$ or with the eigenvalues $\varepsilon_i$ of Eq. (8). We also anticipate that Eq. (22), when applied to calculations of many-electron systems such as atoms, clusters and molecules, will produce reasonable results for the energy gap separating the occupied and empty states. In the case of solids, we expect that the energy gap at various high-symmetry points in the Brillouin zone of semiconductors and dielectrics can also be reproduced.

V. CONCLUSIONS

We have presented the self consistent version of the density functional theory, which allows to calculate the ground state and dynamic properties of finite multi-electron systems.
An exact functional equation for the effective interaction, from which one can construct the action functional, density functional, the response functions and excitation spectra of the considered systems, has been outlined. We have shown that it is possible to calculate the single particle excitations within the framework of DFT. The developed equations permit the calculations of the single particle excitation spectra of any multielectron system such as atoms, molecules and clusters. We also anticipate also that these equations when applied to solids will produce quite reasonable results for the single particle spectra and energy gap at various high-symmetry points in the Brillouin zone of semiconductors and dielectrics. We have related the eigenvalues of the single particle Kohn-Sham equations to the real single particle spectrum. In the most straightforward case, when the exchange functional is treated rigorously while the correlation functional is taken in the local density approximation, the coupling equations are very simple. The single particle spectra do not coincide either with the eigenvalues of the Kohn-Sham equations or with those of the Hartree-Fock equations, even when the contribution coming from the correlation functional is omitted.

ACKNOWLEDGMENTS

The visit of VRS to Clark Atlanta University has been supported by NSF through a grant to CTSPS. MYaA is grateful to the S.A. Shonbrunn Research Fund for support of his research. AZM is supported by US DOE, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research.
REFERENCES

[1] P. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1965); W. Kohn and L.J. Sham, Phys. Rev. A 140, 1133 (1965); W. Kohn, P. Washishta, in: Theory of the Inhomogeneous Electron Gas, eds. by S. Lundqvist, N.H. March (Plenum, New York and London, 1983) p. 79; T. Garbo, T. Kreibich, S. Kurht, E.K.U. Gross, in: Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation, ed. by V.I. Anisimov (Gordon and Breach, Tokyo, 1998).

[2] V.A. Khodel, V.R. Shaginyan, and V.V. Khodel, Phys. Rep. 249, 1 (1994).

[3] E. Runge and E.K.U. Gross, Phys. Rev. Lett. 52, 997 (1984).

[4] V.R. Shaginyan, Solid State Comm. 55, 9 (1985); M.Ya. Amusia and V.R. Shaginyan, J. Phys. B 25, L345 (1992); M.Ya. Amusia and V.R. Shaginyan, J. Phys. II France 3, 449 (1993).

[5] M.Ya. Amusia and V.R. Shaginyan, Phys. Lett. A 269, 337 (2000); M.Ya. Amusia and V.R. Shaginyan, Physica Scripta 68, C10 (2003); M.Ya. Amusia, V.R. Shaginyan, and A.Z. Msezane, Physica Scripta T 68, C133 (2003).

[6] V.R. Shaginyan, Phys. Rev. A 47, 1507 (1993).

[7] D. Ceperly and B. Alder, Phys. Rev. Lett. 45, 566 (1980).

[8] L.D. Landau, Sov. Phys. JETP 3, 920 (1957).