

Theory of the condensed state in a system of excited atoms

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(Submitted 31 May 1982; resubmitted 10 November 1982)

Zh. Eksp. Teor. Fiz. **84**, 442–453 (February 1983)

The condensed excited state (CES) produced as a result of collectivization of excited electrons in atoms, molecules, or impurity centers in solids is investigated theoretically. The transition to the CES is similar in many respects to the Mott insulator-metal transition, and the condensed phase itself possesses many of the characteristic features of semiconductor electron-hole liquids. At high excitation levels of the condensing atoms, exchange and correlation effects are significant, and the density of the electron liquid in the CES is strongly inhomogeneous. The quasiequilibrium CES is investigated by the methods of the pseudopotential and density-functional theory.

PACS numbers: 31.50. + w, 31.20.Tz

In 1968 L. V. Keldysh¹ predicted a metal-like phase in a system of excitations. The new phase was a condensed state of elementary excitations in semiconductors, similar to the hydrogen atom. This electron-hole (EH) liquid was soon observed in experiments, and recently the study of the EH phase has become one of the most interesting and promising trends in solid-state physics.^{2,3} An electron-hole liquid makes it possible to simulate relatively simply a number of extremal states such as the limit of strongly compressed matter which is realized perhaps only in the cores of stars. It is also easy to investigate the spin-polarized phase by applying magnetic fields that are attainable by the usual experimental techniques.

We have shown in brief communications^{4,5} that in a system of excited atoms and molecules of gases, or of impurity centers in various media, the interaction between excited electrons makes possible formation of a condensed phase analogous to the EH liquid in semiconductors. Such a phase can be obtained in two ways: either as the product of the decay of a strongly non-ideal plasma, or as a result of condensation of excited atoms¹⁾ into a condensed excited state (CES). It is quite obvious that the condensed phase is energywise favored for an aggregate of excited atoms, just as is the situation usually in a system of unexcited atoms. The energy gain results in this case from delocalization of electrons and from the decrease of the average kinetic energy per electron of the system. It is also possible to estimate qualitatively the excited-atom density N_n at which the CES are produced, by using the known Mott criterion while the insulator-metal transition:

$$N_n^{1/3} a_n \geq c_n^{-1}, \quad (1)$$

where a_n is the Bohr radius of the n th excited state and c_n is a number of the order of unity. It can be seen therefore that the CES has a lower density the higher the excitation level of the atoms of the condensed phase.

The electron liquid of a CES has a number of unique properties: the density of the CES electrons at high excitation levels corresponds to very large parameters $r_s \gg 1$, where r_s is the radius of a sphere containing one electron and is expressed in atomic units. This electron liquid is strongly non-ideal, since the kinetic energy, which is proportional to r_s^{-2} , is much less than the potential energy $\propto r_s^{-1}$, and the

principal role in it is assumed by correlation and exchange effects. It is known, for example, that in the presence of a spatially homogeneous positive compensating background, owing to exchange and correlation effects, a homogeneous electron distribution is not at all favored, so that the system goes over into a phase with charge-density waves, or undergoes Wigner crystallization.^{6,7} In addition, with increasing excitation level the spatial homogeneity of the electron density of the CES increases. Whereas for lower excitation levels the inhomogeneity can be taken into account by perturbation theory, for the higher levels the inhomogeneity plays a fundamental role. In particular, in a strongly inhomogeneous non-ideal electron liquid one can expect the exchange and correlation effects, which contribute to localization of the electrons in the region of the largest overlap of the wave functions of the excited atoms, to make the CES lifetime longer than the lifetime of an isolated excited atom. Thus, in a number of cases the CES realize another limit of nonideal and inhomogeneous low-density Fermi liquids than of the EH liquid. We emphasize that these features of the CES electron liquid necessitate a different approach to the description of the properties of a condensed excited (CE) phase than in the case of an EH liquid.

The purpose of the present paper is the construction of a theoretical formalism for the description of the properties of a condensed phase of excited atoms, and the determination, on this basis, of the parameters of the CES for certain excitation levels in gaseous and condensed media. We present also a comparative analysis of the general properties of the CE phase and discuss methods of its production.

§1. MOTT TRANSITION IN A SYSTEM OF EXCITED ATOMS

Assume a lattice of a large number of atoms excited to one and the same level n . We bring the atoms gradually closer together to certain finite distances between them. If the atoms were unexcited, then, as is well known, in such a system, at interatomic distances smaller than or of the order of several Bohr radii, the so-called Mott transition into the crystalline state would take place (under the condition that the unit cell contains an odd number of electrons). An exactly similar phenomenon will be observed in a system of excited atoms, and the indicated transition into the metallic state

takes place at densities that are smaller the higher the excitation level n .

The critical distance between the atoms, $a_c^{(n)}$, at which the transition into the collective phase takes place can be determined, just as for the ground state, by using the tight-binding model. We use hereafter Mott's reasoning.⁸ The transition into the crystalline state takes place under the condition that the hopping energy $E_h^{(n)}$, which is determined by the energy of the ground state of the electron in the conduction band in the tight-binding model, is larger than the energy of formation of the polar state $E_p^{(n)}$. The energy of the polar state is defined in the following manner: for the n th excited state the ionization energy is $E_I^{(n)}$, and when a detached electron is attached to another atom in the same excited state, the binding energy $E_B^{(n)}$ is released, from which it follows that $E_p^{(n)} = E_I^{(n)} - E_B^{(n)}$. For the energy, generated by one atomic s level, of hopping into the s band and for the simplest cubic lattice we have (see, e.g., Refs. 9 and 10):

$$E_h^{(n)} = 12\gamma^{(n)}(a), \quad (2)$$

where the energy due to the overlap of the wave functions of two neighboring excited atoms located at a distance a from each other, is given by the expression

$$\gamma^{(n)}(a) = - \int \varphi_n^*(r-a) H \varphi_n(r) dr. \quad (3)$$

Here H is the Hamiltonian of a system consisting of the operators of the kinetic energy and of the electron-ion interaction, and $\varphi_n(r)$ are the atomic orbitals of the level n . According to Mott's hypothesis, if

$$12\gamma^{(n)}(a) \geq E_p^{(n)}, \quad (4)$$

the condensed phase made up of the system of the given atoms is a metal. Solving the last inequality, we obtain a critical value $a_c^{(n)}$ such that if $a < a_c^{(n)}$ the inequality (4) is automatically satisfied. Here $a_c^{(n)} = c_n a_n$, where a_n is the Bohr radius of the n th excited state and c_n is determined by the numerical solution of the equation $E_h^{(n)} = E_p^{(n)}$ for each excitation level. In particular $c_1 \approx 4$ for the ground state of the hydrogen atom we have. For the excited states, c_n is likewise of the order of several units. By the same token we obtain the criterion (1) for the onset of a Mott transition in a system of excited atoms.

There are, however, most important differences between Mott transitions in systems of excited and unexcited atoms. If, besides the excited atoms, the system contains also a large number of unexcited atoms, the formation of a metallic phase sets in at a density lower than that given by condition (1), for in such a system resonant transfer of excitation takes place from atom to atom. This leads to a transfer of the excitations into regions of space where the condition (1) is satisfied and where metallic-phase clusters, which are energywise favored, will be produced.

Thus, a condensed metallic phase consisting of excited atoms is formed when condition (1) is satisfied. This raises the question of describing the equilibrium properties of such a phase. This problem is solved in the next sections.

§2. ENERGY OF CONDENSED EXCITED STATE

If a CES is observed in a system of excited atoms or molecules of a gas or of excited donors in semiconductors, the collective liquid, i.e., the one belonging to the entire system of charged centers, is the electron liquid. If the CES is observed in a system of excited acceptors in semiconductors, the collective system is a hole liquid. Hereafter, without specifying the type of Fermi liquid, we shall use a single term—electron liquid.

At high excitation levels one should expect spatial inhomogeneity of the electron density. Hubbard¹¹ developed methods that make it possible in principle to describe the properties of both a homogeneous and an inhomogeneous Fermi liquid, but they are rather complicated for practical calculations. The most suitable turned out here to be the method of density functionals, developed by Hohenberg, Kohn, and Sham.^{12,13} They have proved that the ground-state energy of an electron-ion system, being a functional of the electron density, reaches its minimum at a density corresponding to its true spatial distribution. Most useful in this case is the system of reducing the nonlocal exchange and correlation interaction between the electrons, to a certain local effective interaction.^{13,14}

A direct extension of the density-functional methods to the description of the properties of the excited states encounters great practical difficulties.¹⁵ The point is that the density functional corresponds to a minimum only at a density equal to the electron density in the ground state of the atoms. To find the spatial distribution of the electrons in this excited state it is necessary to know the distributions of the electron density for all the lower-lying excited states.

This difficulty, however, can be overcome by combining the methods of the density-functional theory with the pseudopotential concept. Our task is to calculate the "pseudodensity" of the electron liquid, i.e., to find a smoothed quantity that coincides with the true distribution of the density outside the atomic cores (outside the "cores" of the pseudopotentials of the given excited state of the atoms). It turns out here that the pseudodensity functional is determined by the pseudopotential uniquely if, as in the usual variant of the theory of density pseudopotentials, one considers the case of nondegenerate states of the system. A proof of this statement is given in Appendix I. We note here that, in accord with Ref. 15, to calculate the electron density distribution in all of space it is necessary, as before, to know the density of the electrons of the low-lying excited states, but now this information is included in the scheme for finding the pseudopotential. It is precisely the introduction of the latter which makes it possible to search for the solution of the variational problem among the class of functions orthogonal to the functions that belong to all the states of the atomic core.

Thus, the equilibrium properties of the CES will be described by using the methods of pseudopotential theory and density functionals. The CES energy will be written out here under the assumption that the temperature contributions are small. The latter can be included without fundamental difficulties within the framework of the computation scheme developed below.¹⁴

Let $v_n(\mathbf{r})$ be the pseudopotential of the system of excited atoms and $\rho_n(\mathbf{r})$ the pseudodensity²⁾ of the valence electrons of the condensate. The energy $E\{\rho_n\}$ of the condensed phase is then a single-valued functional of the density $\rho_n(\mathbf{r})$ and is defined by the expression³⁾:

$$E\{\rho_n\} = T\{\rho_n\} + \frac{1}{2} \int \frac{\rho_n(\mathbf{r})\rho_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}\{\rho_n\} + \int \rho_n(\mathbf{r})v_n(\mathbf{r}) d\mathbf{r}. \quad (5)$$

$T\{\rho_n\}$ is a functional corresponding to the kinetic energy of the electrons. The second term in (5) is the energy of the direct Coulomb electron-electron interaction, the third is the functional of the exchange-correlation electron-electron interaction, while the last one is the energy of the electron-ion interaction.

The energy exchange and correlation functional is determined by the energy of the interaction of electrons of the system with the charges of the exchange-correlation holes¹²⁻¹⁸:

$$E_{xc}\{\rho_n\} = \frac{1}{2} \int \frac{\rho_n(\mathbf{r})\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (6)$$

where ρ_{xc} is the charge density of the exchange-correlation hole,

$$\rho_{xc}(\mathbf{r}, \mathbf{r}') = \rho_n(\mathbf{r}')G(\mathbf{r}, \mathbf{r}'). \quad (7)$$

Here $G(\mathbf{r}, \mathbf{r}')$ is the electron correlation function. We consider below in detail three schemes for calculating the properties of the CES, based on different approximations of these functionals. We shall use the concept of the spherical Wigner-Seitz cell customarily used in the theory of metals.

3. APPROXIMATION OF HOMOGENEOUS ELECTRON LIQUID

The simplest and most fully developed as applied to an electron liquid is the approximation of a homogeneous electron liquid. In this case the density ρ_n^h of the electrons of the CES is associated with the radius of a sphere containing a single electron: $4\pi r_s^3 \rho_n^h / 3 = 1$. We represent the pseudopotential of the ion system in the form of a sum over the direct-lattice vectors \mathbf{R}_j :

$$v_n(\mathbf{r}) = \sum_j v_{nj}(\mathbf{r}-\mathbf{R}_j). \quad (8)$$

The pseudopotential $v_{nj}(\mathbf{r})$ of an individual excited atom can be chosen in the form of the well-known single-parameter Ashcroft pseudopotential^{19,20}

$$v_{nj}(\mathbf{r}) = \begin{cases} 0, & r < R_n \\ -1/r, & r > R_n \end{cases}. \quad (9)$$

The choice of the parameter R_n should lead to an energy spectrum that coincides with the true energy spectrum of the electron in the field of the given ion. In Appendix II is given a procedure for calculating the parameter R_n of the pseudopotential (9) for different excitation levels of a hydrogenlike atom. Using (9) we obtain for the energy per electron of the system a well-known expression¹⁹ (first-order perturbation theory in the pseudopotential):

$$E(r_s) = E\{\rho_n^h\} / \rho_n^h V = \frac{1.105}{r_s^2} + \left[-\frac{0.9}{r_s} + \frac{1.5R_n^2}{r_s^3} \right] - \frac{0.458}{r_s} + \varepsilon_c(r_s), \quad (10)$$

where V is the volume of the system. The first term in (10) is the kinetic energy per electron, the term in the square brackets comes from the second and fourth terms in the right-hand side of (5), and the last two terms in (10) are the energy of exchange and correlation of a homogeneous electron gas. There are several approximations^{21,22} for the correlation energy; for $r_s \leq 5$ it is customary to use the Nozières-Pines expression,²² and for large r_s the Wigner expression is convenient.^{21,23}

The homogeneous-electron-gas approximation is justified if the excitation levels of the atoms that make up the condensed states are not too high. Indeed, the average density of the valence electrons inside an atomic core ($r < R_n$) is as a rule less than outside the core.¹⁹ In the quasiclassical approximation, according to Refs. 4 and 19, the density of the valence electrons inside the core $\rho_n(r < R_n)$ is of the order of $\rho_n(r > R_n) / 2R_n^{1/2}$. Since $R_n^{1/2}$ is of the order of unity for low excitation levels, the inhomogeneity of the spatial distribution of the density can be neglected. For high excitation levels, however, when $R_n^{1/2} \gg 1$, the homogeneous-electron-gas approximation is no longer suitable.

The equilibrium value of the parameter r_s , which coincides in the homogeneous-electron-gas approximation with the radius of the Wigner-Seitz cell R_A , is obtained by minimizing $E(r_s)$,

$$\partial E(r_s) / \partial r_s |_{R_A} = 0. \quad (11)$$

The binding energy B_n per CES atom is obtained from the equation

$$B_n = E(R_A) - I_n, \quad (12)$$

where I_n is the electron binding energy on the n th excited level of the isolated atom. In the hydrogenlike model we have $I_n = -(1/2)n^2$.

Table I lists the CES parameters calculated in the homogeneous-electron-gas model for hydrogenlike-atom excitation levels $3 < n < 5$ (see also Ref. 5). The table will be discussed in Sec. 5 below.

4. INHOMOGENEOUS-ELECTRON-LIQUID APPROXIMATION

For sufficiently high excitation levels, the homogeneous-electron-gas approximation is not valid. Thus, for example, even for the level $n = 5$ the electron density of the CES has a characteristic scale of variation $\rho_n(r < R_n) / \rho_n(r > R_n) \sim 0.1$ over the Wigner-Seitz cell. It is therefore necessary to approximate the functionals in (5) by a

TABLE I

n	R_n	R_A	$-E(R_A)$, eV/at	$-I_n$, eV/at	$-B_n$, eV/at
3	7	12	2.71	1.51	1.20
4	16	26	1.24	0.85	0.39
5	30	48	0.67	0.544	0.13

different scheme that makes it possible to take into-account the effects of the inhomogeneity of the spatial distribution. The simplex approximation is here the local-density approximation.¹²⁻¹⁸

Since we are interesting in effects due to the inhomogeneity of the electron liquid, it is advantageous to calculate the CES energy by using certain model representations for the electron density $\rho_n(\mathbf{r})$. Let R_A be the radius of the Wigner-Seitz cell. For high excitation levels, when $R_n^{1/2} \gg 1$, the average density of the valence electrons differs noticeably from zero near the cell boundary, $\rho_n(r < R_n) / \rho_n(r \approx R_A) \ll 1$. We specify the electron density distribution over the cells by the following trial function:

$$\rho_n(\mathbf{r}) = \rho_0 \exp[-(r - R_n - \Delta_n)^2 / \Delta_n^2], \quad (13)$$

where $\Delta_n = R_A - R_n$. The coefficient ρ_0 is obtained from the condition that the cell contain one ion and one valence electron. For high excitation levels, when effects connected with the inhomogeneity of the electron density are significant, we have the following small parameter:

$$(\Delta_n / R_n) \ll 1. \quad (14)$$

In this approximation we find that

$$\rho_0 = \frac{1}{2\pi^{3/2} R_A^2 \Delta_n} \left(1 + \frac{2\Delta_n}{\pi^{1/2} R_A} \right).$$

Using (13) and taking (14) into account we obtain the following approximate expressions for the terms in the total energy per electron of the condensed phase:

$$T = \frac{0.44}{(R_n^2 \Delta_n)^{3/2}} \left(1 - \frac{0.34 \Delta_n}{R_n} \right) + \frac{1}{4\Delta_n^2} \left(1 - \frac{1.13 \Delta_n}{R_n} \right), \quad (15)$$

$$E_H = \frac{0.5}{R_n} \left(1 - \frac{0.23 \Delta_n}{R_n} \right), \quad (16)$$

$$E_{xc} = -\frac{0.56}{(R_n^2 \Delta_n)^{3/2}} \left(1 - \frac{0.14 \Delta_n}{R_n} \right), \quad (17)$$

$$E_{ei} = -\frac{0.84}{R_n} \left(1 - \frac{0.29 \Delta_n}{R_n} \right), \quad (18)$$

where T , E_{ei} , E_H , and E_{xc} are the kinetic, electron-ion, Hartree, and exchange-correlation energies per electron. Retaining the principal term in the expression for the energy $E_n(\Delta_n) = T + E_H + E_{xc} + E_{ei}$, i.e., the largest contributions in powers of $1/\Delta_n$ of each of the factors (15)–(18), we find in this approximation that

$$E_n(\Delta_n) = \frac{1}{4\Delta_n^2} - \frac{0.56}{(R_n^2 \Delta_n)^{3/2}} - \frac{0.34}{R_n}. \quad (19)$$

Hence, varying E_n with respect to Δ_n , we find that the equilibrium value of the parameter Δ_n^* is given by

$$\Delta_n^* = 1.8 R_n^{2/3}. \quad (20)$$

Substituting Δ_n^* in (15)–(18) we can obtain the energy per electron of the CES at equilibrium. The binding energy per atom of the condensed phase is obtained from (12) by making the substitution $E(R_A) \rightarrow E_n(\Delta_n^*)$. The results of the calculation for the excitation levels $5 < n < 9$ are given in Table II.

It can be seen from the general expression for the energy (19) that the correlation and exchange effects tend to compress the electron liquid: the gain in exchange energy and

TABLE II

n	R_n	R_A	$-E_n$, eV/at	$-I_n$, eV/at	$-B_n$, eV/at
5	30	37	0.95	0.544	0.40
6	45	53	0.68	0.378	0.30
7	65	75	0.50	0.278	0.22
8	90	101	0.38	0.213	0.17
9	120	132	0.30	0.168	0.13

correlation energy is larger the higher the density. Compression of the electron liquid takes place near the repelling cores of the pseudopotential. However, compression increases the kinetic energy, so that it is the competition of these two energy contributions which establishes a certain equilibrium value Δ_n^* (Fig. 1).

A more exact scheme that takes into account the correlation and exchange effects in an electron liquid with fast spatial density oscillations is the nonlocal-density approximation described in detail in Refs. 16–18. Inasmuch as in the general case the pair correlation function of the electron gas is unknown, this function is usually chosen parametrically in the same form as for a homogeneous electron gas, but the parameters of this function at each point of space are chosen from the integral sum rules for it.^{17,18}

The nonlocal-density formalism was used by us to verify the calculations performed in the local-density approximation for a CES produced at the excitation level $n = 9$. The electron-density distribution $\rho_n(\mathbf{r})$ was specified by the function (13) in the interval $(0, 2R_A)$, where $\Delta_n^* = 12.2$ according to (20). In this case the exchange-correlation energy obtained for electron was $E_{xc} = -0.25$ eV, which agrees, accurate to the small parameter (14), with the results of the local calculation for the given excitation level. The kinetic energy in the nonlocal approximation practically coincides in this case with the results of the local calculation. In addition, the exchange-correlation potential of the electron interaction over the Wigner-Seitz cell is obtained numerically (see below). This result was used to determine the total cell potential (see Fig. 2 below).

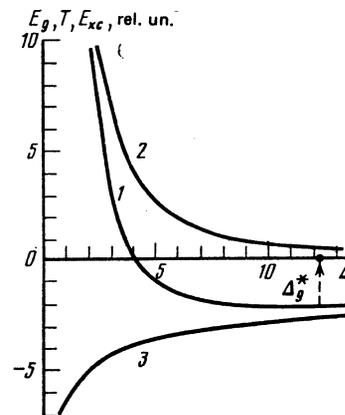


FIG. 1. Dependence of the energy of the condensed excited state E_g (1), of the kinetic energy T (2), and of the exchange-correlation energy E_{xc} (3) on the parameter Δ of the electron-density distribution function at $n = 9$.

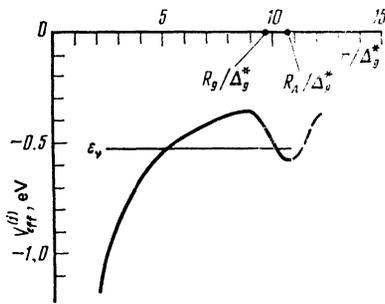


FIG. 2. Effective cell potential (25) for CES electrons ($n = 9$).

We wish also to emphasize here the following circumstance. Just as for metals, the following rule “works” for the CES:

$$B_n \approx T_{\text{CES}} - T_{\text{at}}, \quad (21)$$

i.e., the binding energy is the difference between the average kinetic energy in the condensed phase and the average kinetic energy in the isolated atom. In this sense, the appearance of a binding energy in the CES is explained, as usual, as being due to delocalization of the electrons and to the decrease of their average kinetic energy. This is seen from the data listed in Table III.

5. DISCUSSION OF RESULTS

We proceed to discuss the results obtained in the preceding sections. Tables I and II given the Wigner-Seitz cell radii R_A and the binding energies B_n . It can be seen that the binding energy per CES atom, for different excitation levels, can greatly exceed, for example, the energy kT corresponding to room temperature. Consequently at not too high excitation levels the CES are quite stable formations similar apparently to liquid metals, and the densities of these metal-like formations are close to those of gas. This notwithstanding, the CES can be transparent in the visible band, owing to the low density of their valence electrons. Thus, for the excitation level $n = 9$ we have an estimated plasma frequency $\omega_p = (3/R_A^3)^{1/2} \approx 0.03$ eV.

The surface properties of the condensed phase are quite interesting. It is known²⁴ that the surface energy is defined as the energy needed to divide the crystal into two parts by a single plane passing over the atomic bonds. It should be noted that calculations of the CES surface energy is quite complicated, since great importance is assumed here by questions connected with the spatial distribution of the electron liquid near the phase boundary. We can therefore confine

TABLE III

n	T_{at} , eV	T_{CES} , eV Eq. (15)	$ B_n $, eV Eq. (21)	$ B_n $, eV “exact” calculation
5	0.544	0.132	0.41	0.40
6	0.378	0.096	0.28	0.30
7	0.278	0.070	0.21	0.22
8	0.213	0.057	0.16	0.17
9	0.168	0.044	0.12	0.13

ourselves to an estimate of the surface tension of the condensed phase, using the formula

$$\sigma^{(n)} \approx |B_n| / \pi R_A^2. \quad (22)$$

From this we obtain, say for the excitation level $n = 9$, the estimate $\sigma^{(9)} \approx 0.14$ erg/cm². By way of comparison we indicate that the surface tension of liquid helium is 0.36 erg/cm².

A substantial question is that of the lifetime of the CES. First to take place are radiative transitions to lower-level atomic states. However, a large number of radiative transitions, and in some cases all of them, can be completely forbidden. To this end it is necessary that the transition frequencies be lower than the CES plasma frequency. But besides the rotational decays in this collective phase an important role is played by Auger processes. If they turn out to be principal, the lifetime should decrease greatly. The kinetics of the decay of the CE phase on account of Auger processes is a separate complicated problem and will not be considered here.

The situation changes radically, however, when CES are produced at high excitation levels, when a substantial role is assumed by effects connected with the inhomogeneity of the electron liquid. In accordance with Refs. 13 and 14, we represent the density $\rho_n(\mathbf{r})$ as a sum over the occupied states:

$$\rho_n(\mathbf{r}) = \sum_{\nu} |\psi_{\nu}(\mathbf{r})|^2, \quad (23)$$

where $\psi_{\nu}(\mathbf{r})$ are the solutions of the single-particle Schrödinger equation

$$\left[-\frac{\nabla^2}{2} + v_n(\mathbf{r}) + V_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \psi_{\nu}(\mathbf{r}) = \epsilon_{\nu} \psi_{\nu}(\mathbf{r}). \quad (24)$$

Here $V_H(\mathbf{r})$ is the Hartree potential and $v_{xc}(\mathbf{r}) = \delta E_{xc} \{ \rho_n \} / \delta \rho_n(\mathbf{r})$ is the exchange-correlation potential.¹²⁻¹⁴ It can be verified that in the atomic-core region $|\mathbf{r} - \mathbf{R}_j| < R_n$ the exchange-correlation interaction $v_{xc}(\mathbf{r} - \mathbf{R}_j)$ is much weaker than in the region of space where the electron density differs noticeably from zero. Thus, in the local-density approximation the exchange-correlation potential vanishes exponentially within the atomic core (see also Ref. 4). It follows from (24) that the effective potential in which the valence electron of the CE phase moves is determined by the sum of the cell potentials

$$V_{eff}^{(j)} = v_{ei}(\mathbf{r} - \mathbf{R}_j) + V_H(\mathbf{r} - \mathbf{R}_j) + v_{xc}(\mathbf{r} - \mathbf{R}_j), \quad (25)$$

where $v_{ei}(\mathbf{r})$ is true potential of the electron-ion interaction. We emphasize that (24) contains in place of $v_{ei}(\mathbf{r})$ the pseudo-potential of the electron-ion interaction $v_{nj}(\mathbf{r})$, inasmuch as there the procedure for finding the solution of the variational problem on a class of functions orthogonal to all the lower states is carried out by making the substitution $v_{ei} \rightarrow v_{nj}$. Figure 2 shows the result of a numerical calculation, within the framework of the nonlocal-density formalism, of the cell potential (25) for a CES produced at the excitation level $n = 9$. It can be seen that in the region where the electron-density differs substantially from zero the exchange and correlation effects lead to self-trapping of the electrons.⁴⁾ The lifetime of the CES with respect to decay to less excited atoms can be estimated in the WKB approximation, by starting with the lifetime τ_n of an isolated atom at a given excitation level.

This yields

$$t^{(n)} \approx \tau_n \exp \left[-2 \int_{R_1}^{R_2} (2|\epsilon_v - V_{eff}^{(j)}(r)|)^{1/2} dr \right]. \quad (26)$$

The parameters R_1 and R_2 determine here the region of the sub-barrier motion. From this we have for the excitation level $n = 9$ a typical estimate $t^{(9)} \approx 10\text{--}100$ msec. Thus, for high excitation levels the lifetime of the CES can apparently be macroscopically large.

Methods of observing drops of the CE phase can be different, depending on where the CES is observed, and also on the level to which the condensing atoms are excited. The presence of a CE phase can be revealed, for example, by the change of the luminescence spectrum of the material or by passage, through the investigated volume, of radiation whose wavelength is large compared with the wavelengths corresponding to plasma oscillations of the CES electrons.

It appears that it is experimentally simplest to investigate the possibility of formation of a CE phase in condensed media, particularly in semiconductors, by using the known method of investigating EH liquids. For semiconductors, the energy contributed to excitation of the impurity is relatively small. In addition, at any method of obtaining a large number of excited atoms it is necessary not to overheat the material, to prevent the CE phase from evaporating. This problem is also easiest solved for semiconductors by deeply cooling the investigated samples.

Formation of CES in a system of excited impurity centers in semiconductors leads to a change in the properties of the semiconductor as a whole. It is known that with increasing donor density in a semiconductor its dielectric constant ceases to increase linearly, and when a definite density is reached one observes the so-called dielectric collapse.^{25,26} The dielectric collapse occurring when a definite donor density is reached is evidenced by the transition of the donors into a metallized state at this density. A similar phenomenon should be observed also in a system of excited impurities in semiconductors.⁵⁾ Recently Godik and Petrov²⁸ investigated the photodielectric effects on excited states of Ga impurities in Ge. They observed experimentally a superlinear increase of the dielectric constant of the crystal with increasing density of the excited impurities. These experiments offer evidence of the presence of drops of a condensed excited phase in the semiconductor.³²

In conclusion, the authors thank L. V. Keldysh for discussions and support, V. L. Ginzburg, Yu. V. Gulyaev, E. G. Maksimov, R. A. Suris, I. P. Stakhanov, A. M. Afanas'ev, Yu. A. Bykovskii, M. I. Ryazanov, and V. I. Perel' for a discussion and interest in the work, and G. A. Levacheva for great help with the computer calculations.

APPENDIX I

Hohenberg and Kohn proved the following theorem: for a given external potential $V_0(\mathbf{r})$ the exact distribution of the electron density $\rho_0(\mathbf{r})$ minimizes the energy of the ground nondegenerate state E_0 , which is a single-valued functional of the density $r_0(\mathbf{r})$.¹² This theorem was expanded to include also the case of nonlocal potentials.²⁹ A direct extension of

the results of Ref. 12 to describe excited states¹⁵ greatly complicates the calculation procedures, since it calls for knowledge of the distribution of the electron density for all the low-lying states of the potential. This is actually due to the fact that the solution of the Schrödinger equation for excited states is constructed on a class of wave functions that are orthogonal to all the low-lying states. This is precisely the situation encountered in metal theory when the orthogonalization of the wave functions of the valence electrons to all the wave functions of the inner shell is taken into account by introducing a pseudopotential.¹⁹ A pseudopotential can therefore be introduced also for the description of excited states of quantum-mechanical systems, so that a specified excited state in the field of the pseudopotential turns out to be the ground state.³⁰ We note that in metal theory the density-functional formalism was already used in conjunction with the concept of the pseudopotential.^{14,31} Thus, if we introduce a pseudopotential for a given excited state and the solutions are nondegenerate it is possible, following Refs. 12 and 19, to introduce in the field of the latter a pseudodensity functional such that an exact distribution of the pseudodensity will minimize the energy of the given excited state of the system.

APPENDIX II

In the present paper we use the model pseudopotential proposed by Heine and Abarenkov.¹⁹ It is well known that the most exact calculations on the basis of the pseudopotential can be carried out by fitting its parameters to the experimentally known values of determined parameters of metals.¹⁹ If, however, the parameters of the pseudopotential are determined from first principles, i.e., from data on free atoms, then the accuracy of the calculations is usually 10–20%. For CES the only possibility of determining the parameters of the pseudopotential is at present the use of data on excited atoms. If we use the known compensation theorem,¹⁹ it remains to determine for the model pseudopotential a single parameter—the radius of the “atomic core.”²⁰ To determine this parameter (the radius R_n) a variational procedure was used to find such R_n that the energy levels in the Ashcroft pseudopotential [see (9)] coincided with the corresponding energy levels of the excited hydrogenlike atoms, $J_n = -(1/2)n^2$. The trial wave function used was Gaussian and similar to (13). The result was $R_n = 7, 16, 30, 45, 65, 90$ and 120 for the respective levels $n = 3, 4, 5, 6, 7, 8$, and 9 .

We note that the pseudopotentials include formally also the effects of exchange in correlation between the valence electrons and the inner-shell electrons (if the latter exist).

¹⁾By “excited atoms” are meant everywhere also electron-excited molecules, impurity centers, etc., unless otherwise stipulated.

²⁾This quantity will hereafter be called density.

³⁾We use the atomic system of units throughout.

⁴⁾The situation has a classical analog (pointed out to the authors by L. V. Keldysh), which explains the nature of the exchange-correlation interaction that leads to the onset of an effective potential well in the region where the CES electrons are localized. Let a test charge be located inside a sphere uniformly charged over the surface. Although in this case there is no field inside such a sphere without the test charge, in the presence of

the latter inside the sphere there are induced on the sphere image charges and the test charge will be attracted to its own image by a polarization interaction with it.

⁵See Ref. 27 concerning the influence of frequency dispersion of the dielectric constant on the carrier interaction.

- ¹L. V. Keldysh, Proc. 9th Internat. Conf. on Semicond. Physics (Moscow), Nauka, 1968, p. 1302; in: Excitons in Semiconductors [in Russian], Nasuka, 1971.
- ²V. L. Ginzburg, Usp. Fiz. Nauk **134**, 469 (1981) [Sov. Phys. Usp. **24**, 585 (1981)].
- ³T. M. Rice, Sol. St. Phys. **32**, 1 (1977); J. C. Hensel, T. G. Phillips, and G. A. Thomas, *ibid.* p. 88.
- ⁴E. A. Manykin, M. I. Ozhovan, and P. P. Poluektov, Dokl. Akad. Nauk SSSR **260**, 1096 (1981) [Sov. Phys. Dokl. **26**, 947 (1981)].
- ⁵E. A. Manykin, M. I. Ozhovan, and P. P. Poluektov, Ukr. Fiz. Zh. **27**, 448 (1982); Zh. Tekh. Fiz. **52**, 1474 (1982) [Sov. Phys. Tech. Phys. **52**, 905 (1982)].
- ⁶A. W. Overhauser, Adv. Phys. **27**, 343 (1978).
- ⁷K. Utsumi and S. Ichimaru, Phys. Rev. **B24**, 3220 (1981).
- ⁸N. F. Mott, Metal-Insulator Transitions, Barnes & Noble, 1974.
- ⁹N. W. Ashcroft and N. D. Mermin, Solid State Physics, HR&W, 1976, Vol. 2.
- ¹⁰W. A. Harrison, Solid State Theory, McGraw, 1970.
- ¹¹J. Hubbard, Proc. Roy. Soc. **A240**, 539 (1957); **A243**, 336 (1958); **A244**, 199 (1958).
- ¹²P. Hohenberg, and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ¹³W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

- ¹⁴A. K. Rajagopal, Adv. Chem. Phys. **41**, 59 (1979).
- ¹⁵A. K. Theophilou, J. Phys. C, **12**, 5419 (1979).
- ¹⁶O. Gunnarson, M. Jonson, and B. I. Lundqvist, Phys. Rev. **B20**, 3136 (1979).
- ¹⁷J. A. Alonso and L. A. Girifalco, Phys. Rev. **B17**, 3735 (1978).
- ¹⁸J. A. Alonso and L. C. Balbas, Phys. Lett. **81A**, 467 (1981).
- ¹⁹V. Heine, M. Cohen, and D. Ware, Pseudopotential Theory [Russ. Transl.], Mir, 1973.
- ²⁰N. W. Ashcroft, Phys. Rev. Lett. **23**, 48 (1965).
- ²¹D. Pines, Elementary Excitations in Solids, Benjamin, 1963.
- ²²D. Pines and P. Nozières, The Theory of Quantum Liquids, Vol. 1, Benjamin, 1966.
- ²³E. Wigner, Phys. Rev. **46**, 1002 (1934).
- ²⁴N. D. Lang and W. Kohn, Phys. Rev. **B1**, 4555 (1970).
- ²⁵J. R. Bose, H. B. Shore, and L. M. Sander, Phys. Rev. **B21**, 3037 (1980).
- ²⁶T. G. Castner, Phys. Rev. **B21**, 3523 (1980).
- ²⁷E. A. Manykin, M. I. Ozhovan, and P. P. Poluektov, Teor. Mat. Fiz. **49**, 283 (1981).
- ²⁸V. I. Bocharikov, E. E. Godik, and A. V. Petrov, 2nd Republic Conf. on Photoelectric Phenomena in Semicond., Abstracts, Kiev, Naukova Dumka, 1982, p. 63.
- ²⁹T. L. Gilbert, Phys. Rev. **B12**, 2111 (1975).
- ³⁰Y. Sakai and S. Huzinaga, J. Chem. Phys. **76**, 2537 (1982).
- ³¹G. P. Kerker, Phys. Rev. **B24**, 3468 (1981).
- ³²E. A. Manykin, M. I. Ozhogin, and P. P. Poluektov, in Ref. 28, p. 169.

Translated by J. G. Adashko