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Finite size atom: The new quasiparticle in the self-consistent Hartree–Fock approximation

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ABSTRACT

It is shown that, in the self-consistent quantum statistical Hartree–Fock approximation, the number of electronic states localized on one nucleus is finite. This result is obtained on the basis of the general electron–nuclear model of matter and provides convergence of the atomic statistical sum and finiteness of the "atom" size. In general approach the characteristic size of the "atom" is a function of density and temperature. However, it is shown, that in a wide range of thermodynamic parameters, for relatively low temperatures, characteristic orbits and electron energy eigenvalues are independent of density and temperature. In this case, the sizes of the orbits are of order of the Bohr radius which is a minimal characteristic size in the system for typical parameters of plasma with atomic states.

1. Introduction

Real matter (gases, liquids, solids, plasma) is constructed from nuclei and electrons interacting with each other according to the Coulomb law [1]. It would be very desirable, based on the known nucleus charge as an initial problem parameter and, based only on the Coulomb law, to construct a scheme for calculating macroscopic properties of different media. The consistent approach to implement such a scheme is based on the methods of the diagram technique of the perturbation theory [1,2]. The main difficulties in the realization of this approach are caused by the necessity of the simultaneous consideration of both "localized" states of electrons and nuclei ("atoms", "molecules", etc.), whose description requires accurate summation of rows of the perturbation theory, and "delocalized" states which are quite successfully described within the lowest orders of the perturbation theory [1,2]. As a result, "localized" states for weakly nonideal plasma are considered within the second virial coefficient [1–4]. In this case, there arises the known problem of the convergence of the statistical sum of the hydrogen atom, which is directly related to its size [2]. A large number of works are devoted to the solution of this problem, where various procedures and physical mechanisms of "cutoff" of the statistical sum of the atom were proposed, including the papers [5–12] which have already become classical (see [1–3] and references therein for more details). In this case, the following circumstance is very surprising. As is known [13,14], the self-consistent Hartree–Fock approximation and its various generalizations are basic in calculations of the structure and energy spectra of atoms and molecules in quantum chemistry. Despite the known statement that the self-consistent Hartree–Fock approximation is the best single-particle approximation in quantum statistics [15], it is almost not used in the study of thermodynamic properties of Coulomb systems, where "localized" states should be taken into account [1]. This Letter is devoted to the solution of the problem of convergence of the statistical sum of the hydrogen atom and its size finiteness, based on the self-consistent quantum-statistical Hartree–Fock approximation for the Coulomb system.

2. Two-component electron–nuclear plasma: Adiabatic approximation and classification of the electron states

We consider the two-component Coulomb system (CS) in volume V at temperature T within the canonical ensemble consisting of electrons (subscript e) and nuclei (subscript c), taking into account the quasineutrality condition $\sum_{a=e,c} z_a e n_a^{(0)} = 0$. Here $n_a^{(0)} = \langle N_a \rangle^{(can)}/V$ is the average density of the number of particles; N_a is the operator of the total number of particles of type a, characterized by mass m_a, the average density of the number of particles n_a, and charge $z_a e$; angle brackets $\langle \cdots \rangle^{(can)}$ mean averaging over the canonical ensemble. For such a CS, the Hamiltonian $H^{CS} = H_{ee} + H_{cc} + H_{ec}$ in the secondary quantization representation is written as [1]

$$H_{aa} = -\frac{\hbar^2}{2m_a}\int \psi_a^+(\mathbf{r})\nabla^2\psi_a(\mathbf{r})\,d\mathbf{r} + V_{aa},$$

$$H_{ec} = \int u_{ec}(\mathbf{r}_1 - \mathbf{r}_2)N_e(\mathbf{r}_1)N_c(\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2, \qquad (1)$$

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$$V_{aa} = \frac{1}{2}\int u_{aa}(\mathbf{r}_1-\mathbf{r}_2)\psi_a^+(\mathbf{r}_1)\psi_a^+(\mathbf{r}_2)\psi_a(\mathbf{r}_2)\psi_a(\mathbf{r}_1)\,d\mathbf{r}_1\,d\mathbf{r}_2,$$

$$u_{aa}(r) = \frac{z_a z_b e^2}{r}. \tag{2}$$

Here $u_{aa}(r)$ is the potential of the Coulomb interaction of particles of types a and b, $\psi_a^+(\mathbf{r})$ and $\psi_a(\mathbf{r})$ are the field creation and annihilation operators, $N_a(\mathbf{r}) = \psi_a^+(\mathbf{r})\psi_a(\mathbf{r})$ is the density operator of the number of particles of type a, which, in the coordinate representation, is written as $N_a(\mathbf{r}) = \sum_{i=1}^{N_a}\delta(\mathbf{r}-\mathbf{R}_i^a)$. The values $\mathbf{R}_i^a$ are the coordinates of particles of type a. We emphasize that the total number of particles N_a of each type in the canonical ensemble is specified and is the C-number, $N_a = \int N_a(\mathbf{r})\,d\mathbf{r} = \langle N_a\rangle^{(can)}$. The free energy F^{CS} of the considered quasi-neutral CS consisting of the set number of electrons N_e and nuclei N_c in volume V at temperature T, $F^{CS} = -T\ln \mathrm{Sp}\{\exp(-\frac{H^{CS}}{T})\}$, in the adiabatic approximation for nuclei, is written as

$$F^{CS} \cong -T\ln \mathrm{Sp}_c\left\{\exp\left(\frac{F_{ec}-H_{cc}}{T}\right)\right\},$$

$$F_{ec} = -T\ln \mathrm{Sp}_e\left\{\exp\left(-\frac{H_{ee}+H_{ec}}{T}\right)\right\}. \tag{3}$$

The quantity F_{ec} (3) is the free energy of the subsystem of electrons being in the external field of stationary nuclei. In this case, the operator of the density of the number of nuclei $N_c(\mathbf{r})$ in the Hamiltonian H_{ec} (1) is the C-number. At this stage, when considering the subsystem of electrons in the external field of stationary nuclei, we proceed from the equivalence of the large canonical and canonical ensembles, i.e., we suppose that the equality [16]

$$F_{ec} = \Omega_{ec} + \mu_e\langle N_e\rangle^{(GE)},$$

$$\Omega_{ec} = -T\ln \mathrm{Sp}_e\left\{\exp\left[-\frac{H_{ee}+H_{ec}-\mu_e N_e}{T}\right]\right\}, \tag{4}$$

for the free energy F_{ec} (3) is valid. In (4) the function Ω_{ec} is the thermodynamic potential of the subsystem of electrons with the chemical potential μ_e in the external field of stationary nuclei, whose value depends on the nucleus coordinates $\{\mathbf{R}_i^c\}$ as the external parameters, $\langle N_e\rangle^{(GE)}$ is the average number of electrons as a function of temperature T, volume V, and chemical potential μ_e. In this case, the quasineutrality condition takes the form $\langle N_e\rangle^{(GE)} = z_c N_c$ and is used to determine the chemical potential μ_e of electrons.

Then, to describe the field operators $\psi_a^+(\mathbf{r})$ and $\psi_a(\mathbf{r})$ in the representation of occupation numbers [13], it is required to choose a complete set of wave functions $\langle\mathbf{r}|\{Q\sigma\},\{\mathbf{R}_i^c\}\rangle$ characterizing single-particle electronic states with the energy $E(\{Q\})$

$$\psi_e^+(\mathbf{r}) = \sum_{\{Q\sigma\}}\left\langle\{Q\sigma\},\left\{\mathbf{R}_i^c\right\}\middle|\mathbf{r}\right\rangle a_{\{Q\sigma\}}^+,$$

$$\psi_e(\mathbf{r}) = \sum_{\{Q\sigma\}}\left\langle\mathbf{r}\middle|\{Q\sigma\},\left\{\mathbf{R}_i^c\right\}\right\rangle a_{\{Q\sigma\}}, \tag{5}$$

in the external field of nuclei. Here $a_{\{Q\sigma\}}^+$ and $a_{\{Q\sigma\}}$ are the creation and annihilation operators of electrons in the state $\langle\mathbf{r}|\{Q\sigma\},\{\mathbf{R}_i^c\}\rangle$, $\{Q\sigma\}$ is the set of quantum numbers, including the spin number σ (hereafter, for simplicity, spin indices are not considered). In the problem under consideration the set of coordinates $\{\mathbf{R}_i^c\}$ of nuclei plays the role of eigenvalue parameters. In this case, single-particle electronic states in the external field of nuclei are classified into two groups [17]. One (A) is localized (subscript "loc") states characterized by exponential spatial decrease with distance from localization centers. Among them are the single-center bound states of electrons in atoms, two-center ones in molecules, etc. Another group (B) is delocalized (subscript "del") states in which the electron propagates throughout the system. The typical example of delocalized states are plane waves $\langle\mathbf{r}|\mathbf{q}\rangle$, $\langle\mathbf{r}|\mathbf{q}\rangle = (1/\sqrt{V})\exp(i\mathbf{q}\mathbf{r})$, $\epsilon(q) = \frac{\hbar^2 q^2}{2m_e}$ which describe the behavior of the free electron with momentum $\hbar\mathbf{q}$ and energy $\epsilon(q)$. Thus, in the optimum case, the complete set of wave functions for the representation (5) should describe both localized and delocalized states of electrons. However, there are many problems in this way. The first problem is "physical"; it is associated with the fact that localized electronic states vary as thermodynamic parameters of the CS are varied; this leads, in particular, to the Mott effect [18], i.e., disappearance of localized states. This means that the quantum-mechanical consideration is insufficient for determination of localized states; quantum statistics effects should also be considered. The second problem, to the solution of which this Letter is devoted, is associated with the necessarily finite number of electronic states localized on one center. By the example of the hydrogen atom considered within quantum mechanics ignoring quantum statistics effects [13], it is known that the number of bound electronic state is infinite, which leads, in turn, to the divergence of not only the statistical sum for an individual atom, but also to the unlimited atomic size at any nonzero temperature [2]. Based on combinatory reasons, E. Fermi [7] has shown that the introduction of the finite size of atoms results in an exponential limitation of the statistical sum. It is easy to see that the statistical sum limitation to any maximum value of the principal quantum number $n_{\max}$ is also a simultaneous introduction of the finite size of the atom. The absence of limitation, i.e., the case $n = \infty$, is the case corresponding to an infinite-size atom, which is meaningless (the size of the n-th orbit of the hydrogen atom is $R_n = n^2 a_0$, where is the Bohr radius) [19]. Hence, it is impossible to correctly use the "single-center" (in the sense of the localization center) approximation in the description of localized states. In this case, the transition to the "single-center" approximation is meaningful when the condition

$$\langle R_a\rangle \ll \langle r\rangle_c, \quad \langle r\rangle_c = \left(\frac{4\pi n_c}{3}\right)^{-1/3}, \tag{6}$$

is satisfied, where $\langle R_a\rangle$ is the "atom" size and $\langle r\rangle_c$ is the average distance between nuclei (see below).

The consideration of the quantum statistics effects (with the opportunity to pass to the thermodynamic limit) means that localized electronic states for a separated nucleus should be considered taking into account that the CS, as a system of many identical particles, contains many other electrons (electronic states). However, the multiplicity of noninteracting electrons is already formally taken into account in the used formalism of secondary quantization (1), (2), (5).

The divergence directly follows from the definition of the electron distribution function $f_e(E(\{Q\}))$ in states $\langle\mathbf{r}|\{Q\},\{\mathbf{R}_i^c\}\rangle$ with energy $E(\{Q\})$

$$f_e(E) = \left\langle a_{\{Q\}}^+ a_{\{Q\}}\right\rangle^{(GE)} = \left\{\exp\left(\frac{E-\mu_e}{T}\right)+1\right\}^{-1},$$

$$\langle N_e\rangle^{(GE)} = \sum_{\{Q\}} f_e(E), \tag{7}$$

when using energy levels of the hydrogen atom as energies. It remains to hope that the "effective" consideration of the electron–electron interaction while retaining the single-particle consideration will make it possible to solve the problem of the finite number of bound states in the "atom", i.e., in the "single-center" approximation for wave functions (it is clear that the "multicenter" problem for localized electronic states is in principle unsolvable),