

Electronic spectrum of a metal containing hydrogen-atom impurities

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The question of bound electrons around a proton in a metal is analyzed on the basis of a calculation of the electronic energy of the system in the approximation of a self-consistent Hartree field for the bound electrons with allowance for the effects associated with the many-particle nature of an electronic liquid in the formation of the bound electron states. Calculation of the energy of the electronic structures with one and two bound electrons around the proton shows that these structures are favored above the state of the electronic system arising upon screening of the charge by only free electrons.

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Interest in the problem about the electronic structure around a proton in metals arose a long time ago,^[1] shortly after Mott's prediction of the effect of the screening of the field of an impurity by free electrons.^[2] The exchange corrections to the Mott potential were later^[3] taken into account. If the estimates of Sachs and Goepert-Mayer^[1] led to the possibility of an electron's capture in a bound state of the proton, Mott's conclusion^[2] was different. Owing to the enhancement of the screening of the proton field as a consequence of interelectronic exchange, the discrete level vanished over the entire range of metallic densities of the electrons. Layzer^[4] has shown that the discrete solutions of the one-particle effective equation, similar to the solutions obtained in^[1,3], are related to hole-type excitations of the electronic liquid.

The concept of the ionization of the hydrogen atom in a metal has been maintained in the literature up to the present time (see, as an example,^[5]); meanwhile simple estimates show that two bound electrons may exist in the screened field of a proton.^[6] In the present work a calculation is made of the energy of a metal's electronic system in the presence of and in the absence of bound electrons near the impurity proton.

First of all we note a common deficiency of the previous investigations, in that the quantitative estimates were made with the enlistment of an effective potential for the electron located at the Fermi surface. In this connection it was implied that the screening of the impurity charge takes place only by free electrons. It is clear, however, from physical considerations that in the case of localization of the electron in a bound state around the proton, the potential field acting on it is substantially changed as a consequence of the different character of the screening of the impurity center proton-bound electron by the free electrons.

Having in mind an investigation of the situation involving the bound electrons of a proton in a metal, let us isolate in the spirit of the Hartree method the one-particle localized orbitals in the wave function of the electronic system:

$$\Psi_1(1, 2, 3, \dots, N+1) \approx \varphi(1) \Phi_1(2, 3, \dots, N+1), \quad (1a)$$

$$\Psi_2(1, 2, 3, \dots, N+1) \approx \det[\varphi_1(1), \varphi_2(2)] \Phi_2(3, \dots, N+1). \quad (1b)$$

The wave function (1a) is written for the case of a single bound electron, and the wave function (1b) is for two bound electrons near the proton; φ , φ_1 , and φ_2 are the orbitals of the bound electrons, and Φ_1 and Φ_2 are the wave functions of the free electrons. The spatial and

spin coordinates of the i -th electron are denoted by the corresponding numbers in Eqs. (1a) and (1b). There are N electrons of the initial metal plus one electron of the hydrogen atom in the system.

As is well known, the true wave function of an electronic system is antisymmetric under interchange of the coordinates of any pair of electrons. In the approximate writing of the system's wave function (1a) and (1b), this property is violated for the bound electron-free electron pair, but is preserved for the coordinates of two electrons in a qualitatively identical state: bound or free. Here the many-particle wave function, without any separation of the one-particle states, is written down for the free electrons. All this leads to a result beyond the framework of the Hartree approximation and allows one to take account of collective effects of the electronic liquid in the formation of electronic states localized on the impurity. The changes and contributions, which arise upon taking account of the permutational symmetry of the wave function with respect to the coordinates of the bound-free electrons (which is achieved by taking an antisymmetric linear combination of functions of the form (1a) or (1b)) will be discussed at the end of the article.

The theory of metals, developed in recent years,^[7,8] reduces to an expansion of the energy of the electron-ion system in powers of the pseudopotential. In this connection, a complete account of the contributions of the electron-electron interaction is taken in each order of the expansion. In essence this theoretical scheme is the opposite of that employed in the single-electron theory. If this scheme is enlisted in order to investigate the electronic structure around a proton in the lattice of a metal, the zero order approximation in the pseudopotential will correspond to a model of a metal with the charge of the metallic ions uniformly smeared out over space and the fixed proton with bound electrons isolated in this background. The subsequent terms of the expansion, taking the discrete nature of the crystal lattice into consideration, are expressed in the form of lattice sums over the sites in reciprocal space and represent corrections to the characteristics, due to the presence of the proton and the bound electrons on the proton. This is a consequence of the relative smallness of the components of the pseudopotential and the square of the absolute value of the bound electron's wave function even on the sites nearest to zero. Therefore, in the following we shall, for the sake of simplification, confine our attention to an investigation of the problem based on the uniform model of a metal. It should be noted that

the previous investigations of the problem^[1,3,4] were carried out in the framework of precisely this model. Therefore, the model with a uniform background has self-sustaining interest.

In the assumed model the Hamiltonian for the electrons has the form

$$H = -\frac{1}{2} \sum_i \nabla_i^2 \delta(\sigma_i, \sigma_i') - \sum_i \frac{\delta(\sigma_i, \sigma_i')}{r_i} - \sum_i \int \frac{\rho_0 d\mathbf{r}'}{|\mathbf{r}_i - \mathbf{r}'|} \delta(\sigma_i, \sigma_i') + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \delta(\sigma_i, \sigma_i') \delta(\sigma_j, \sigma_j'). \quad (2)$$

Conventional notation is used in Eq. (2), the meaning of the terms is well known (ρ_0 is the charge density of the background), and the Hamiltonian is written in atomic units.

We can find the wave functions of the bound electrons by starting from a variational principle.^[9] For this purpose it is necessary to calculate the average value of the energy of the electron system using the trial wave functions (1a) and (1b) (their normalizability is assumed). In this connection, in the case of a single bound electron around the proton we have

$$E_1 = -\frac{1}{2} \int \varphi'(\mathbf{r}) \nabla^2 \varphi(\mathbf{r}) d\mathbf{r} - \int \frac{|\varphi(\mathbf{r})|^2}{r} d\mathbf{r} - \int \int \frac{\rho_0 |\varphi(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{1}{2} \int \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} d\mathbf{r} - \int \frac{\rho \varphi(\mathbf{r}, \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \rho(\mathbf{r}, \mathbf{r}) \left(-\frac{1}{r} + \int \frac{|\varphi(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) d\mathbf{r} + \int \int \frac{\gamma(\mathbf{r}, \mathbf{r}; \mathbf{r}', \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (3)$$

where $\rho(\mathbf{r}, \mathbf{r}')$ and $\gamma(\mathbf{r}, \mathbf{r}'; \mathbf{r}_1, \mathbf{r}'_1)$ denote, respectively, the one-particle and two-particle density matrices of the free electron gas. The first three terms in expression (3) correspond to the kinetic and potential energies of the bound electron in the field of the proton and the positive background of the metal ions; the remaining terms correspond to the energy $E_1^{\text{el.liq.}}$ of the electronic liquid of the metal's free electrons in the background of the ions in the presence of the external field,^[10] resulting from the presence in the metal of a defect in the form of a proton with a bound electron.

In order to determine the wave function of the bound electron, it is necessary to solve the variational problem for the minimum value of the functional E_1 . Here the energy $E_1^{\text{el.liq.}}$ should have the smallest value, and consequently must be the energy of the ground state of the free electrons of the metal in the field of the impurity hydrogen atom. As a consequence of this, $E_1^{\text{el.liq.}}$ has a functional dependence on the wave function of the bound electron. At the present time there are a number of theoretical schemes for calculating the energy of an electronic liquid in an external field with the enlistment of perturbation theory (see, for example,^[11]). However, the most systematic method is the scheme of Brovman and Kagan.^[7] We write their result, obtained upon taking complete account of the contributions of the electron-electron interaction and the terms up to second order of the perturbations in the external field, in the form

$$E_1^{\text{el.liq.}} = N\bar{\epsilon} - \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{V_{\mathbf{k}} V_{-\mathbf{k}}}{\epsilon(\mathbf{k})} \pi(\mathbf{k}), \quad (4)$$

where $\bar{\epsilon}$ is the average energy per electron in the electronic liquid^[12] in the absence of the defect, $\pi(\mathbf{k})$ and $\epsilon(\mathbf{k})$ are the polarization operator and the static dielectric constant function of the electron gas, and $V_{\mathbf{k}}$ is the Fourier component of the external field. In our case

the external field with respect to the free electrons is determined by the next to the last term in formula (3). The electrical neutrality of the entire system has been taken into account in the derivation of expression (4). At the same time the energy of the proton's interaction with the positive background of the metal ions is also taken into consideration. As a result, the terms containing the charge density ρ_0 of the background vanish.

We note that the smallness parameter of the expansion (4) of the energy $E_1^{\text{el.liq.}}$ is the very small (in our case) ratio $e^2/\Omega^{1/3}\epsilon_F$ (see^[7]; e is the elementary charge; ϵ_F is the energy of a free electron at the Fermi surface, and Ω is the volume of the system). However, an immediate conclusion about the smallness of the subsequent (after the second) orders of the energy expansion would be premature, since the number of terms of a given order increases in proportion to N^n (n denotes the order of the contribution to the energy). The smallness of the contribution arises as a result of a partial cancellation of terms of the same order due to the appearance of phase factors in them. The results of calculations of the physical characteristics of metals^[13,14] allow one to estimate the third-order contribution to the energy as approximately equal to 0.1 of the second-order contribution. Therefore, calculation of the third-order term in the expansion cannot lead to a qualitative change of the following results. However, investigation of the second-order terms has a fundamental character and leads to a semiquantitative description of the physical situation, relating to the electronic structure of an impurity hydrogen atom in a metal.

Extending the result for the case of a single bound electron, expressed by formula (3), to the case of other electronic structures around the proton, let us write the Fourier component of the external field in the form

$$V_{\mathbf{k}} = \int d\mathbf{r} e^{i\mathbf{k}\mathbf{r}} \left(-\frac{1}{r} + \int \frac{n_1 |\varphi_1(\mathbf{r}')|^2 + n_2 |\varphi_2(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \quad (5)$$

where n_1 and n_2 are numbers taking the values 0 and 1. In the case $n_1 = n_2 = 0$ we have a structure without bound electrons; for $n_1 = 1, n_2 = 0$ a single bound electron exists on the proton; two bound electrons exist for $n_1 = n_2 = 1$.

Substituting (5) into relationship (4), we obtain an expression for the energy of the free electrons, which are being subjected to the influence of the impurity proton, atom, or negative ion of hydrogen. Summing this expression with the terms for the energy of the bound electrons, we obtain the total energy of the electronic system for a metal containing an impurity. Let us write this energy in the form

$$E_{0,1,2} = \left(N+1 - \sum_{i=1,2} n_i \right) \bar{\epsilon} + \frac{1}{2} v(0) + \mathcal{E}_{1,2}, \quad (6)$$

$$\mathcal{E}_{1,2} = \sum_{i=1,2} n_i \left[-\frac{1}{2} \int \varphi_i'(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) d\mathbf{r} - \int \left(\frac{1}{r} + v(\mathbf{r}) \right) |\varphi_i(\mathbf{r})|^2 d\mathbf{r} + \frac{1}{2} \int |\varphi_i(\mathbf{r})|^2 v(\mathbf{r} - \mathbf{r}') |\varphi_i(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' \right] \quad (7)$$

$$+ n_1 n_2 \iint |\varphi_1(\mathbf{r})|^2 \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + v(\mathbf{r} - \mathbf{r}') \right) |\varphi_2(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' \quad (8)$$

$$v(\mathbf{r}) = - \sum_{\mathbf{k} \neq 0} \left(\frac{4\pi}{k^2} \right)^2 \frac{\pi(\mathbf{k})}{\epsilon(\mathbf{k})} e^{i\mathbf{k}\mathbf{r}}.$$

In expressions (6) and (7) the subscript 0 refers to the

case when there are no bound electrons around the proton, the subscript 1 refers to the case of a single bound electron, and the subscript 2 refers to the case of two bound electrons around the proton in the metal. The function $v(\mathbf{r})$ has the meaning of the potential energy function of a test charge in the field of the excess density of electrons, screening the proton's charge in the absence of bound electrons.

The meaning of the various terms in expression (6) is as follows. The first term describes the change in the energy of the free electrons, associated with either the removal of a single electron from the collective body of electrons in the metal and its capture as a second bound electron in an orbit around the proton or with the addition of the hydrogen atom's electron to the collective body of free electrons. In this connection the average energy $\bar{\epsilon}$ per electron in the electronic liquid also somewhat changes its value (by an amount $\sim 1/N$) due to the change in the average distance between the electrons. Upon multiplication of this change by N , we have a finite contribution to the energy, which must be taken into consideration along with the energy $\bar{\epsilon}$. The second term in expression (6)—this is the energy of the proton's screened interaction with the polarization field of the electronic liquid, which is caused by the presence in the metal of the proton itself. The last term—the quantity $\mathcal{E}_{1,2}$ —expresses the binding energy of a single, localized electron around a proton in a metal, measured from the zero value in vacuum, or the binding energy of two localized electrons around a proton, also with respect to the vacuum state. The first two integral terms in expression (7) for $\mathcal{E}_{1,2}$ describe the contributions of the kinetic and potential energies of the bound electrons to the proton's field screened by the free electrons. The next integral expression is the energy of the interaction of each of the bound electrons with the polarization potential of the free electrons, induced by the intrinsic field of the bound electron. This interaction leads to the effect of self-trapping of the localized electron. The last term in expression (7) represents the energy of the screened interaction of the bound electrons among themselves.

It is interesting to note that the interaction of the charge with the polarization field of the free electrons caused by it enters into expression (7) with a factor $1/2$ of the value obtained for the electrostatic interaction of the charges. The factor $1/2$ is related to taking account of the positive energy contribution of the electron-electron interaction associated with the formation of the screening shell of free electrons.

The solution of the variational problem on the minimum for the functional $\mathcal{E}_{1,2}$ under the assumption of normalizability of the wave functions determines both these functions of the bound states of electrons near a proton in a metal and the energy values of the electronic system associated with one and two bound electrons. Here it should be noted that the theoretical scheme of a self-consistent field, proposed in the present work, differs substantially from traditional schemes^[9] where the single-particle wave functions of each electron in the system are found by a self-consistent method. In our scheme in the case of a single bound electron we have one equation with a self-consistent solution $\varphi(\mathbf{r})$. If the number of discrete levels is greater than one, the discrete eigenvalue spectrum of this equation determines the excitation spectrum of the electronic system

associated with the transition of a bound electron from one quantum state to another. For two bound electrons, we obtain for self-consistency a system of two equations. In this case the electronic structure in which $\varphi_1 \equiv \varphi_2$ possesses the lowest energy. In the case $\varphi_1 \neq \varphi_2$ the functions φ_1 and φ_2 will be orthogonal. If such a solution exists for localized functions, then the symmetric and antisymmetric wave functions for the two bound electrons, constructed as a linear combination of pair products of the single-particle functions, describe the excited state of the system with parallel and antiparallel orientation, respectively, of the spins of the bound electrons.

We calculated the quantum states possessing the lowest energy for the electronic system of a defect metal in the presence of one and two bound electrons around the proton. The results of computer calculations of the energies \mathcal{E}_1 and \mathcal{E}_2 with the aid of a hydrogenlike trial wave function

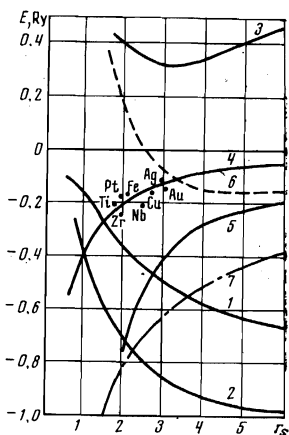
$$\varphi(r) = Z^{3/2} \pi^{-1/2} e^{-Zr}$$

for the ground state, where Z is a variable parameter, are shown in the figure. A range of densities of the electronic liquid, characterized by the parameter r_S (r_S is the radius of the sphere, limiting the volume per electron, in atomic units; for metals $r_S = 1.8$ to 5.5), is investigated which is characteristic of real metals. The exchange and correlation contributions in the calculation of the function $v(\mathbf{r})$ were taken into account according to the scheme of^[8].

From the figure we can see that, although the binding energy of an electron in a localized state decreases with increasing density of the free electrons, nevertheless in the complete range of metallic electron densities this energy remains considerably below the energy of a free electron at the Fermi surface in both the case of a single bound electron on the proton and in the case of two bound electrons. Therefore, states of the electronic system with bound electrons are energetically more favorable. The radii of the bound electrons' wave functions increase somewhat in comparison with the electron state in a free hydrogen atom: by 1.1 times in the case of a single bound electron, and by 1.3 times in the case of two bound electrons.

Curves for the energy of the metal-hydrogen atom system are also shown in the figure. The state when the sample of metal and the unperturbed hydrogen atom are dispersed in space is adopted as the zero value for measurement of the energy. These curves determine the binding energy of the hydrogen atom in metal as a function of the density of free electrons for three different electronic structures around the proton: two bound electrons, one bound electron, and the screening of the proton's charge by the free electrons. The first structure possesses the least energy, and the last possesses the greatest energy.

It is known from experiment that the binding energy of the hydrogen atom decreases in the alkali-noble-transition series of metals and has a negative value. Experimental data on the binding energy of the hydrogen atom is shown in the figure for a number of metals having body-centered cubic (bcc)^[15] and face-centered cubic (fcc)^[16] lattices. The behavior of the binding energy associated with an increase of the free-electron density in the metal is correctly communicated by the curves, pertaining to electronic structures with bound



The energy of the electrons in localized states of a proton and the binding energy of a hydrogen atom in metal as a function of the average distance between the free electrons: curve 1 is for ϵ_1 ; curve 2 is for ϵ_2 ; curves 3, 4, 5 represent the binding energies of a hydrogen atom in metal in the cases of the following electronic structures, respectively, of the proton: without bound electrons, with one bound electron, and with two bound electrons; curve 6 represents ϵ_F ; curve 7 represents $v(0)/2$. The dots correspond to the experimental data.

electrons. In this connection the calculation for the state with one bound electron gives an energy closest to the experimental data. The structure without bound electrons around the proton ("ionization" of hydrogen in metals) leads to a positive binding energy of the hydrogen atom with all metals. This result was deduced by Friedel for the case of copper^[5] as an example of a contradiction between theory and experiment in the prediction for the energy of solubility of hydrogen in metals. Furthermore, in contrast to the experimental dependence, the dependence of the binding energy on the density of the electron gas associated with "ionization" of the hydrogen atom in a metal has a minimum in the region of average metallic densities of the electron gas (for $r_s \approx 3$). In principle these contradictions in the theoretical description of the energy of solubility of hydrogen in metals are removed upon consideration of the electronic structures involving bound electrons around the proton.

Transitions of the electronic system between states, characterizing the difference of the electronic structure around the impurity proton, produce characteristic features of the electronic spectrum of a metal containing hydrogen in the lattice. One can assume that these characteristic features of the energy spectrum of the electronic system will appear experimentally in the form of the characteristics of energy loss associated with the passage of electrons, protons, and other charged particles through the metallic crystal containing hydrogen.

In conclusion we note that the scheme employed in the present work can be improved in the spirit of the Hartree-Fock method by writing down linear combinations of functions of the form (1a) and (1b) which have been antisymmetrized with respect to interchange of the coordinates of the bound-free electrons. In this connection exchange terms, analogous to the terms of the Hartree-Fock method, appear in the energy of the system, but in them the collective effects of the electronic liquid are taken into consideration. These terms to some extent compensate the positive energy of repulsion

of the bound electron from the electron shell screening the defect, lowering the energy of the structure with bound electrons and facilitating an enhancement of the localization of the bound electrons. However, this compensation effect is small due to the long-range nature of the Coulomb interaction of the electrons with the proton and among themselves and as a consequence of the smallness of the ratio of the radius d of the orbit of a bound electron to the average distance r_s between free electrons. Besides the named terms, additional terms appear (which are important for $r_s \approx d$), taking account of the correlation effects between bound and free electrons, which corresponds to a result beyond the framework of the Hartree-Fock method. However, it is reasonable to apply the Hartree-Fock approximation together with allowance for the discrete nature of the crystal lattice of a metal.

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