POTENTIAL RELIEF AND QUANTUM STATE OF LIGHT ATOM (HYDROGEN) IN METALS

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Abstract

We compare the results of the many-electron theory of binding energy: \( \Delta \varepsilon_0 \) in the case of the proton and \( \Delta \varepsilon_1 \) in the case of the quasiatomic state. The “scatter ellipse” of the experimental data (altogether 20 points) covers the curve of \( \Delta \varepsilon_1 \) corresponding to the quasiatomic state. The electron structure which arises in the case where the proton is screened only by the free electrons gives a value of the binding energy higher than the experimental values.

Keywords: hydrogen atom, proton, binding energy, quasiatomic state.

The rough evaluation of the energy of the discrete level near a proton in metal can be given within the Thomas–Fermi approximation. In this approximation, the problem is reduced to the calculation of the discrete spectrum of the single-particle Schrödinger equation, including the potential of the impurity center. As was demonstrated by the evaluation, there is a discrete level under the bottom of the conduction band at the density of electron gas \( r_s > 1.8 \) [1] (\( r_s \) is the dimensionless average distance between electrons).

However, this estimate caused serious doubts related to the fact that the simplified Thomas–Fermi model does not make it possible to take correctly into account the contribution of the exchange between electrons to the formation of a discrete level. For this reason, the conclusions from [2] are of considerable interest, where the same problem is considered on the basis of a consistent quantum-mechanical formal description [3, 4]. This work in fact confirmed the initial estimate obtained in the Thomas–Fermi model. In reality, according to [2], at densities \( r_s = 2.07–5 \), which are intrinsic to metals, a small bound state forms under the bottom of the band, which is localized near a proton. (The energy of the discrete level was also studied in [5] in the case of hydrogen in simple metals at the density of electron gas \( r_s > 1.9 \)).

Searches for a solution of the problem on the existence of a discrete level near a proton are possible within a somewhat different approach [6], which is not related to the analysis of the single-particle Schrödinger equation. This approach is based on the analysis of the change in the energy of the system with introduction of a hydrogen atom. A multielectron model of a metal in which the charge of the ion of the lattice is homogeneously “spread” over the bulk electron cell and only the effects of polarization of the electron gas are taken into account is used as a model in it. Deformation “polaron” effects are not considered.

The interaction (binding) energy of hydrogen atoms with metals can be represented as a functional relative to the wave functions of the bound electron \( \varphi_e \):

\[
\Delta \varepsilon_n[\varphi_e] = \varepsilon_F (1-n) + \varepsilon_{(pr)} + n\varepsilon[\varphi_e] - \varepsilon^{(mol)}.
\]

(1)

Here, \( n \) is the occupation number of the discrete level: \( n = 0 \) corresponds to the electron structure without a bound electron near the proton, and \( n = 1 \) corresponds to the quasiatomic state of the hydrogen atom. \( \varepsilon_{(pr)} = \tilde{V}(0)/2 \) is the binding energy of the proton with the metal:

\[
\tilde{V}(r) = -\frac{1}{\Omega} \sum_q \left( \frac{4\pi}{\sigma} \right)^2 e^2 \frac{\pi(q)}{\varepsilon(q)} \exp[i(qr)]
\]

(2)
is the potential of the electron cloud shielding the proton; $\Omega$ is the volume on one junction of the lattice; $\pi(q)$ is the polarization operator; $\varepsilon(q)$ is the statistical dielectric permittivity; and $\varepsilon^{(mol)}$ is the binding energy of atoms in the hydrogen molecule, considered to be the point of reference. The functional $\varepsilon[\varphi_e]$ from (1) determines the energy of the bound electron near the proton in the metal; it corresponds to

$$
\varepsilon[\varphi_e] = -\frac{1}{2m_e} \int \varphi_e^* (r) V^2 \varphi_e (r) \, d\mathbf{r} - \int \varphi_e^* (r) \overline{\nabla} \varphi_e (r) \, d\mathbf{r} - \frac{1}{2} \int \left| \varphi_e (r) \right|^2 \overline{\nabla} \left( |\mathbf{r} - \mathbf{r}'| \right) \left| \varphi_e (r') \right|^2 \, d\mathbf{r} \, d\mathbf{r}',
$$

where $V(r) = e^2 / r + \overline{\nabla} (r)$ is the potential of the shielded proton field and $m$ is the mass of the hydrogen atom.

The critical value of the functionals was sought on the basis of the test hydrogen-like function

$$
\varphi_e (r) = \exp \left( -Zr \right) \left( \frac{\pi}{Z^3} \right)^{1/2}.
$$

As for the exchange, the contribution to the shielding from the exchange interaction between free electrons is taken into account by the representation of the polarization operator, included in $\varepsilon^{(pr)}$ and $\varepsilon[\varphi_e]$ in the form from [7]. The correction from the exchange interaction of the bound electron with free electrons is negligible owing to the small radius of the wave function $\varphi_e$ relative to the characteristic distance between electrons.

The results of numerical analysis of the binding energy $\Delta\varepsilon_0$ in the case of a proton and $\Delta\varepsilon_1$ in the case of the quasimolecular state of a hydrogen atom are given in Fig. 1, where the region in which the experimental values of this measure are distributed is limited by the ellipse. According to the figure, the “concentration ellipse” of experimental data (altogether 20 points) covers the curve $\Delta\varepsilon_1$, corresponding to the quasimolecular state of the hydrogen atom. The electron structure formed upon the shielding of the proton only by free electrons gives higher binding energy than the experimental values. In addition, the trend of the growth in the binding energy with an increase in the electron density does not correspond to the values observed, that is, the trend which is represented by the structure without a bound electron in the range $r_s = 2–3.5$. The indicated increase is determined by the increase in the Fermi level with a growth in the electron density, because the electron of the ionized hydrogen atom goes to the Fermi surface.

Fig. 1. Interaction energy of hydrogen in metals: $\Delta\varepsilon_0$, in the absence of bound electron (proton); $\Delta\varepsilon_1$, in the case of quasimolecular state of hydrogen atom; $\Delta\varepsilon_2$, in the anionic state; $r_s$ is the average distance between electrons. The points are the data of experiments from [8].
LITERATURE


