

Dependence of the Binding Energy of the Metal Crystal Lattice on the Average Number of Conduction Electrons

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Abstract—We establish the dependence of the electron binding energy in a separate isolated Wigner–Seitz cell of the metal crystal lattice on the average number of electrons located in this cell. The calculation is made using the modified Hellmann–Feynman theorem, which allows relating the eigenvalue of the steady-state Hamiltonian to the variation in its parameters that do not affect the degree of freedom of a system. As one of these parameters, we choose the average number of electrons in the cell. According to the calculated data, removal of 10–30% of electrons in monovalent metals leads to the crystal lattice fracture. The results obtained using the Hellmann–Feynman theorem are directly compared with the data of the jellium model.

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1. INTRODUCTION

Metals retain their properties and shape owing to the dynamic equilibrium between the forces of electrostatic interaction of ions with each other and with electrons. This equilibrium is determined by the electroneutrality of the ion–electrons system both in an individual cell and in the entire metal volume. It is the conduction electrons that work as a “glue” ensuring the lattice stability and determine the individual physicochemical properties of metals.

The lattice ions, in their turn, keep electrons within the boundaries of a metal and prevent them from leaving it [1].

The most important parameters characterizing the properties of metals are the total energy, binding energy of conduction electrons, cell size, and average number of electrons in the cell. The direct calculation of the dependence of the binding energy on the average number of electrons in the cell is quite laborious and the result is predetermined by a chosen interaction model. The use of the Hellmann–Feynman theorem [2] makes it possible to obtain the results in a simpler way, which is nearly independent of the greater part of the proposed model. This theorem was used by Feynman [2] to calculate the interaction energy and forces in a molecule at its any configuration.

If the Hamiltonian, which is not explicitly time-dependent, includes parameters that do not determine the degrees of freedom of such a system, then these parameters will affect the energy eigenvalues and eigenfunctions of the system. The Feynman theorem allows establishing the dependence of the Hamilto-

nian eigenvalue on the variation in a separate parameter. Basing on this theorem, the intermolecular interaction forces were calculated as a function of the internuclear distance at the much smaller calculation volume [2].

In this study, we choose parameter λ of the average number of electrons in the metal cell. This parameter determines the binding energy and, consequently, stability of metals under normal conditions.

2. MAIN APPROXIMATIONS

We consider the problem on finding the dependence of the binding energy of conduction electrons located in a separate isolated Wigner–Seitz cell on their average number λ for Li, Na, K, V, Cu, Rb, Ag, and Au metals.

One electron with mass m_e is assumed to carry elementary charge e . If under normal conditions the neutral Wigner–Seitz cell contains n_0 conduction electrons, then after the removal of a part of electrons $q = n/n_0$, the remaining number of electrons will be $\lambda = 1 - q$ and the average mass and charge of the remaining electrons will be $m_e \rightarrow \lambda m_e$ and $e \rightarrow \lambda e$, respectively. Further, the atomic units are used, but Bohr radius a_B chosen as a length scale and the Rydberg constant determining the energy unit are assumed to be independent of the variation in electron parameters (charge and mass). In the calculations, the contributions of the volume and correlation energies are ignored.

The main properties of a metal are determined by the electrons whose energy slightly differs from the Fermi energy E^F

$$E^F = \frac{\hbar^2}{2m} (3\pi^2 n_0)^{2/3}. \quad (1)$$

Upon electron density variation from n_0 to n ($n_0 \rightarrow n = \lambda n_0$), the Fermi energy changes by

$$E_\lambda^F = \lambda^{-1/3} E^F \quad (2)$$

and the corresponding momentum p^F changes by

$$p_\lambda^F = \lambda^{1/3} p^F. \quad (3)$$

The main equation in quantum mechanics is the Schrödinger equation. In writing this equation, the classical correlation between the energy and momentum of an individual microparticle is determined by the operator form using the formal transformations [3]

$$\mathbf{p} \Rightarrow -i\hbar \frac{\partial}{\partial \mathbf{r}}, \quad L_z \Rightarrow -i\hbar \frac{\partial}{\partial \varphi}. \quad (4)$$

Analogously to relations (4), the momentum operator for the nonintegral number of momentum operator particles can be written in the form

$$\mathbf{p}_\lambda \Rightarrow -i\hbar \lambda^{1/3} \frac{\partial}{\partial \mathbf{r}}. \quad (5)$$

The electromagnetic interaction considered below requires the replacements $m \rightarrow \lambda m$ and $e \rightarrow \lambda e$; then, the replacement for the potential energy is $U \rightarrow \lambda U$.

Approximation of the Wigner–Seitz cell by a sphere with radius r_s makes it possible to write the spherically symmetric Schrödinger equation with regard to the conditions at the cell boundaries in the form

$$\{\Delta + \lambda^{1/3} [E_\lambda - \lambda U]\} \psi_\lambda = 0, \quad \left. \frac{\partial \psi_\lambda}{\partial r} \right|_{r=r_s} = 0. \quad (6)$$

Solving Eq. (6), we can find the dependence of the binding energy of conduction electrons on their average number in the Wigner–Seitz cell. The results of the calculations for the model in which the potential energy was approximated by the potential energy of a uniformly charged sphere [4] were reported in [5]. The calculation appeared fairly complex and their results significantly dependent on the chosen approximation of the potential energy in (6).

There is the relation that establishes the dependence of the eigenvalue and wave function of the Hamiltonian on this parameter. This relation is called the Hellmann–Feynman theorem [2, 6] and has the form

$$\frac{\partial E_\lambda}{\partial \lambda} = \int \psi_\lambda^* \frac{\partial H_\lambda}{\partial \lambda} \psi_\lambda d\tau_\lambda + E_\lambda \frac{\partial}{\partial \lambda} \int \psi_\lambda^* \psi_\lambda d\tau_\lambda. \quad (7)$$

Note that there is the difference between the classical formulation of the Feynman theorem [7] and its direct use in this study. This difference is caused by the

wave function normalization condition. For Hamiltonian H_λ depending on parameter λ , the energy and wave function are determined by solving the Schrödinger equation

$$H_\lambda \psi_\lambda = E_\lambda \psi_\lambda, \quad (8)$$

and the wave function meets the normalization condition dependent on the λ value

$$\int \psi_\lambda^* \psi_\lambda d\tau_\lambda = \lambda, \quad (9)$$

whereas the wave function of the electron from the neutral cell satisfies the isolation condition and the last term in the right-hand side of Eq. (7) is usually absent. The total electron energy is usually determined from the ordinary relation

$$E_\lambda = \int \psi_\lambda^* H_\lambda \psi_\lambda d\tau_\lambda, \quad (10)$$

where, according to (5), the dependence of the Hamiltonian on parameter λ is the nonuniform function of this parameter:

$$H_\lambda = \lambda^{-1/3} T_{\lambda=1} + \lambda U_{\lambda=1} = \lambda^{-1/3} T_1 + \lambda U_1, \quad (11)$$

here, T_1 and U_1 are the operators of the kinetic and potential energies for the neutral cell. Substitution of (11) in (7) with regard to Eqs. (9) and (10) leads to the first-order linear equation for the bottom of the conduction band

$$\frac{\partial E_\lambda}{\partial \lambda} = E_\lambda - \frac{1}{3} \lambda^{-4/3} \int \psi_\lambda^* T_1 \psi_\lambda d\tau_\lambda + \int \psi_\lambda^* U_1 \psi_\lambda d\tau_\lambda. \quad (12)$$

Expression (12) is exact and, for direct calculations, we have to choose a model determining the potential energy U of the interaction between conduction electrons and the ionic core and to establish the dependence of wave function ψ_λ on parameter λ .

3. WAVE FUNCTION AND ENERGY OF ELECTRONS UNDER THEIR DEFICIENCY

The state of conduction electrons in the Wigner–Seitz cell is determined by a set of wave functions ψ_1 , where the parameter $\lambda = 1$ corresponds to the condition of its electroneutrality. As electrons remove from the cell ($\lambda < 1$), the interaction energy changes, which leads to the change in the wave function $\psi_1 > \psi_\lambda$. To calculate the energy using Eq. (12), we need in the information about the wave function under electron deficiency. The available models describe the state of an electron in the neutral cell. To find the wave function of electrons under their deficiency, we write it in the form of superposition of the wave functions of the neutral cell

$$\psi_\lambda = \sum_{\alpha} c_{\alpha} \{\psi_1\}_{\alpha}, \quad (13)$$

where α is the set of quantum numbers characterizing the state of electrons in a separate neutral cell. Limit-

ing the consideration to the first term in formula (13), we write the functional

$$G = \int d\tau |\psi_1 - \psi_\lambda|^2 \quad (14)$$

under condition (9). To find the best approximation of the wave function, it is necessary to minimize functional (14), which can be done using the method of Lagrange multipliers μ

$$G = \int d\tau \{ |\psi_1 - \psi_\lambda|^2 + \mu |\psi_\lambda|^2 \}, \quad (15)$$

i.e.,

$$\frac{\delta G}{\delta \psi_\lambda} = 0, \quad \frac{\delta G}{\delta \psi_\lambda^*} = 0. \quad (16)$$

Substitution of (15) in formulas (16) allows finding the correlation between the wave functions in the form

$$\psi_\lambda^* = (1 + \mu)\psi_\lambda^*, \quad \psi_1 = (1 + \mu)\psi_\lambda. \quad (17)$$

Multiplying the left- and right-hand parts of formulas (17) by each other and integrating over the cell volume, we obtain, with regard to normalization conditions (9), the relation between factors μ and λ

$$\frac{1}{1 + \mu} = \pm \sqrt{\lambda}. \quad (18)$$

Finally, in the first approximation, the relation between the wave functions of conduction electrons corresponding to the neutral cell and cell with electron deficiency $q = 1 - \lambda$ is

$$\psi_\lambda = \pm \sqrt{\lambda} \psi_{\lambda=1}. \quad (19)$$

Thus, representation (19) corresponds to the condition of the best approximation of wave functions without using a special model of interaction of electrons with the atomic core. Relation (19) makes it possible to estimate the parameters of metals under electron deficiency based on the information about the parameters of the neutral cell.

We use this relation to estimate the electron energy. In the absence of electron deficiency, the electron energy is determined by minimizing the total energy in the neutral cell ($\lambda = 1$)

$$E_1 = \int \psi_1^* (T_1 + U_1) \psi_1 d\tau_1, \quad (20)$$

where $E_1 = E_{\lambda=1}$ is the energy of the bottom of conduction band of the neutral Wigner–Seitz cell. Upon removal of the relative average number λ of electrons from the cell, the volume of the latter increases in accordance with the relations

$$n_\lambda = \lambda n_{\lambda=1} = \lambda n_1, \quad d\tau_\lambda = \frac{d\tau_1}{\lambda}, \quad (21)$$

where n_λ is the number of electrons in the unit volume of the charged and neutral ($n_1 = n_{\lambda=1}$) cells. Excluding the electron potential energy from formula (12) using relations (20) for the neutral cell and taking into

account its volume variation (21), we arrive at the equation for calculating the energy E_λ of the bottom of the conduction band as a function of the relative number of electrons in a separate cell

$$\begin{aligned} \frac{dE_\lambda}{d\lambda} - E_\lambda &= E_1 - \left\{ 1 + \frac{1}{3\lambda^{4/3}} \right\} \int \psi_1^* T_1 \psi_1 d\tau_1 \\ &= \frac{dE_\lambda}{d\lambda} - E_\lambda = E_1 - \left\{ 1 + \frac{1}{3\lambda^{4/3}} \right\} \bar{T}. \end{aligned} \quad (22)$$

Equation (22) allows us to relate the energy parameters of the charged cell ($\lambda < 1$) to the energy parameters of the neutral cell ($\lambda = 1$).

The use of the Hellmann–Feynman theorem for estimating the parameters of the charged cell allows not only simplifying the calculations, but also extracting those significantly affecting the binding energy of a conduction electron. In particular, instead of the numerical solution of the second-order differential equation with the boundary condition depending on the relative number of electrons λ in the cell [5], the theorem makes it possible to analytically solve Eq. (22) via the average value of its kinetic energy in the neutral cell.

4. COMPARISON OF THE CALCULATED DATA OBTAINED BY SOLVING THE SCHRÖDINGER EQUATION AND USING THE HELLMANN–FEYNMAN THEOREM

To initially estimate the average kinetic energy in formula (22), we use the results of the free electron model, where the main properties of elements are determined by electrons with energies similar to the Fermi energy E^F [8]

$$\bar{T} = \frac{3}{5} E_1^F. \quad (23)$$

Substitution of (23) to formula (22) yields the simple equation for the bottom of the conduction band

$$\frac{dE_\lambda}{d\lambda} - E_\lambda = E_1 + \frac{3}{5} \left\{ 1 + \frac{1}{3\lambda^{4/3}} \right\} E_1^F \quad (24)$$

with the boundary condition

$$E_{\lambda=1} = E_1. \quad (25)$$

The energy E_1 of the bottom of the conduction band cannot be directly experimentally determined in the neutral cell and is estimated from its relation with the energies directly determined in experiments

$$E_1 = \Delta \mathcal{H} + E_a, \quad (26)$$

where E_a is the energy of the lowest state of the metal atom and $\Delta \mathcal{H}$ is the atomization enthalpy. As the average number of electrons in a separate cell increases, the volume of the latter grows, the energy of the bot-

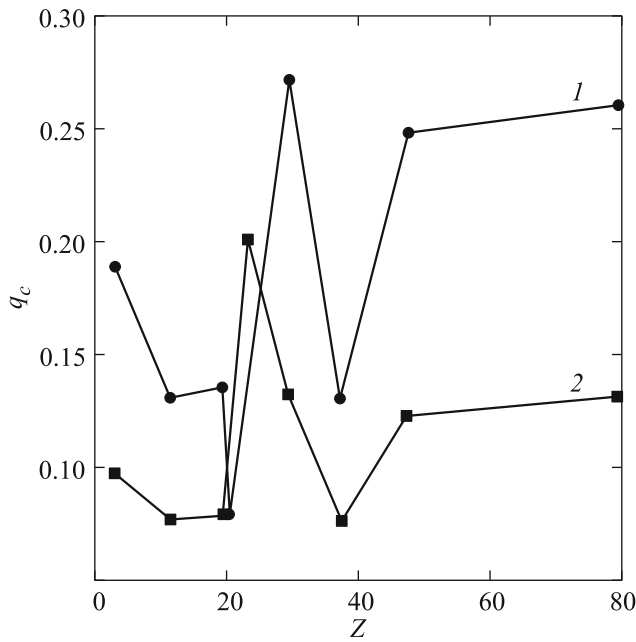


Fig. 1. Atomic number dependence of the critical relative number of removed electrons corresponding to the break of stability of metals. (1) Calculation made in this study and (2) calculation reported in [5].

tom of the conduction band increases, and the metal loses its stability under the condition

$$E_1 = E_a, \tag{27}$$

i.e., the metal decays into separate noninteracting atoms. This process is accompanied by the energy

release called the Coulomb explosion. As was shown in [9], there is the critical number of electrons q_c after removal of which the metal loses its stability. In this case, the total energy of an electron in the cell becomes comparable with energy (27) of an individual atom. Figure 1 shows the calculated dependence of relative number of electrons q_c , after removal of which some metals lose their stability in accordance with (27), on their atomic number Z . For comparison, the figure shows the results of analogous calculations obtained using the jellium model [5] by solving directly the Schrödinger equation with the corresponding edge condition at the Wigner–Seitz cell boundary.

Based on the above-described approach, we calculated the dependence of the electron atomization enthalpy $\Delta\mathcal{H}_\lambda$ on the average number of removed electrons $q = 1 - \lambda$

$$\Delta\mathcal{H}_\lambda \approx E_\lambda - E_a. \tag{28}$$

Figures 2 and 3 show the calculated dependences of enthalpy (28) in Ry units on the average electron deficiency q under the assumption of the isolated cell. It can be seen that metals can be conventionally divided in two groups. The first group involves unstable metals with a relatively low q_c value (Fig. 2) and the second group, the more stable metals with a somewhat higher critical value q_c (Fig. 3). Although the average cell radius r_s is approximately the same for all metals ($3.6 d_B$), all the group-I elements have the body-centered lattice with the low energy of the bottom of the conduction band ($E_1 \sim 0.43$ Ry). The energy of the bottom of the conduction band for Group II metals with the face-centered lattice, except for V, is twice as

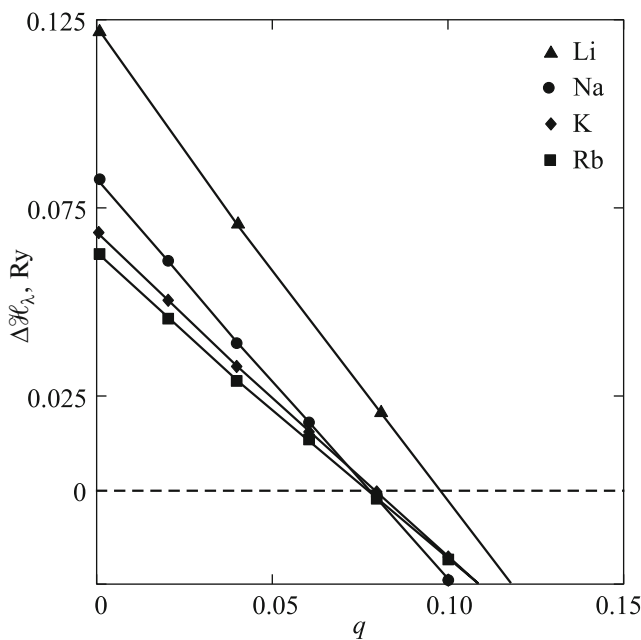


Fig. 2. Enthalpy of atomization of Group I metals.

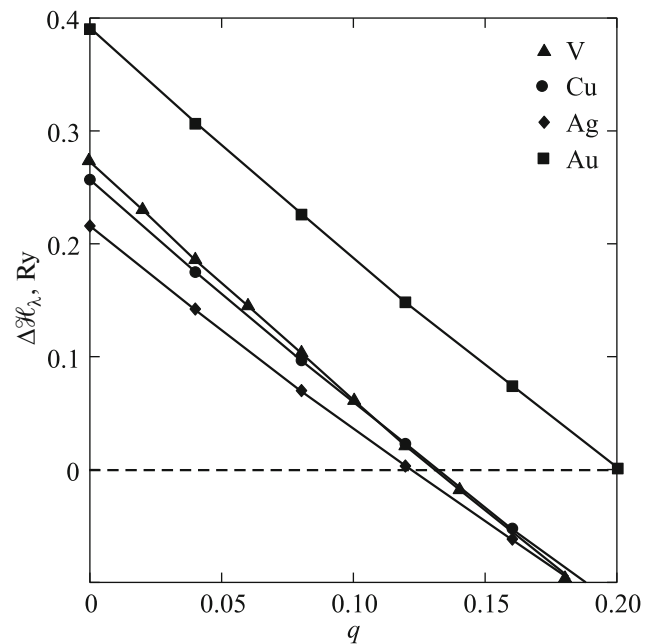


Fig. 3. Enthalpy of atomization of Group II metals.

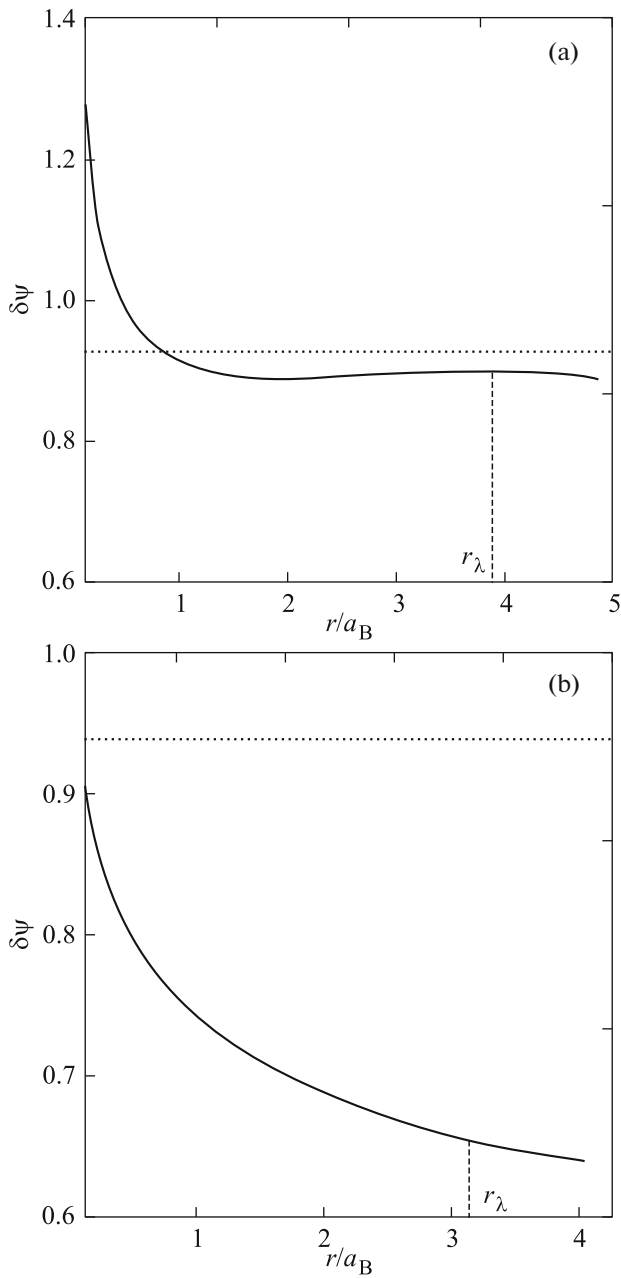


Fig. 4. Ratio $\delta\psi$ of the radial wave functions of an electron for the charged and neutral cells. Calculated data for (a) Na and (b) Cu.

much as for Group I metals ($E_1 \sim 0.85$ Ry), which, according to (26), leads to the higher stability of a metal. To break the stability of these metals, it is necessary to remove the larger (by a factor of about 1.8) number of electrons.

5. DISCUSSION

The main approximation of this model is relation (19) of the electron wave functions in the charged and neutral cells. To check this relation, we solved the

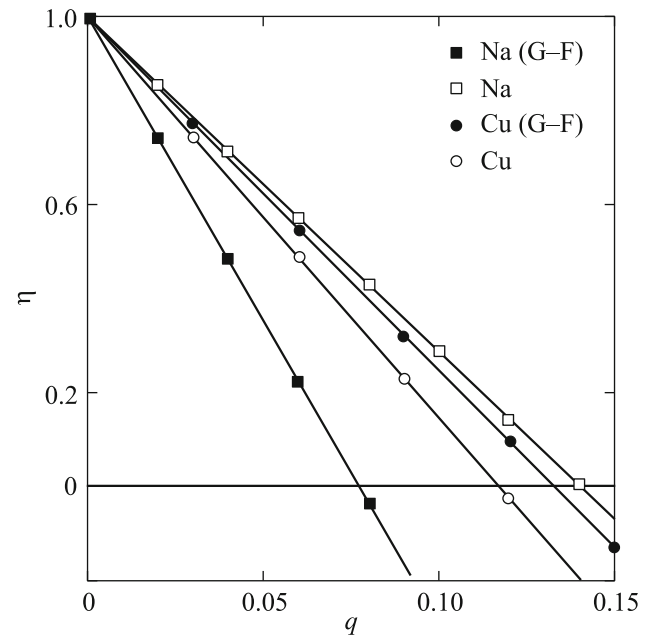


Fig. 5. Dependence of relative atomization enthalpy (29) of Na and Cu on the relative number of removed electrons. Open symbols show the calculation using the jellium model [5] and closed symbols, the calculation made in this study.

problem of finding the wave functions of the neutral and charged cells using the jellium model. The calculated data for two metals are illustrated in Figs. 4a and 4b, which present the relations for the radial wave functions of an electron $\delta\psi = \psi_\lambda/\psi_1$ of the charged and neutral cells for Na (Fig. 4a) and Cu (Fig. 4b). The solid line shows the calculation from [5]. The dashed horizontal line shows the parameter $\sqrt{\lambda}$ for this metal, which corresponds to approximation (19) of this study. The vertical line shows the radii of spheres approximating the charged Wigner–Seitz cells for the corresponding metals.

As can be seen in Fig. 4a, approximation (19) is valid for Na, while for Cu the situation is essentially different (Fig. 4b).

The difference between the wave functions is reflected on the dependence of the atomization enthalpy on the average number of electrons in the cell. Figure 5 presents the calculated ratios between the enthalpies of the charged and neutral cells

$$\eta = \frac{\Delta\mathcal{H}_\lambda}{\Delta\mathcal{H}_{\lambda=1}} \quad (29)$$

on the average number of removed electrons. It can be seen in Fig. 5 that the significant differences between the wave functions in Figs. 4a and 4b do not lead to the large difference between the dependences of the atomization enthalpies for different models. This confirms the possibility of using approximation (19) relating the

wave functions of electrons of the neutral and charged cells.

6. CONCLUSIONS

Based on the Hellmann–Feynman theorem for an isolated Wigner–Seitz cell, we calculated the dependence of the binding energy on the electron deficiency. The results obtained agree well with the data of the jellium model.

It should be taken into account that if the wave functions of electrons are known exactly, the Hellmann–Feynman theorem makes it possible to accurately calculate the dependence of the Hamiltonian eigenvalue on the chosen parameter. The proposed replacement of wave functions (19) under electron deficiency for the wave function without the electron deficiency led to the change in the Hellmann–Feynman theorem, which allowed us to take into account the variations caused by a decrease in the electron density and an increase in the cell volume. This approach allows performing the calculations using not only the free electron approximation, but also other models with the wave functions that can differ from plane waves.

It can be seen in Fig. 1 that the values of parameter q_c for metals from Li to Au lie in the range of $q_c = 0.07–0.27$. According to the results obtained, after removal of 10–11% of electrons on average from a separate isolated cell, the metal atomization accompanied by the energy release occurs [10]. Although the critical electron deficiency estimations obtained in this study agree well with the estimations made in the previous works using other approaches, note that the error of replacement of the electron wave functions in the neutral and charged cells cannot be estimated within the investigated approximation. However, the comparison with the quantum-mechanical calculations showed that for the cubic syngony elements with the body-centered lattices, the approximation of the Wigner–Seitz cell by a sphere and replacement of wave functions (19) are quite satisfactory approximations. For metals with the closer packed face-centered lattices,

the approximations used work worse. The choice of wave functions does not significantly affect the estimated critical number of removed electrons.

The calculations showed that the approximation of the curves in Figs. 2 and 3 by the linear dependences corresponding to the small deficiencies q agrees with the results obtained by solving the Schrödinger equations [5]. This allows estimating the critical number of removed electrons q_c using the intermediate q values.

Despite the assumptions used, the Hellmann–Feynman theorem allows the quite satisfactory estimations to be obtained by simple calculations. In view of the aforementioned, it is interesting to experimentally verify the estimations by studying the inertial explosions of metals under their interaction with a barrier [11].

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