THE POSSIBILITIES OF EXPERIMENTAL VERIFICATION OF QUANTUM THEORIES OF METALS AT THE LEVEL OF TECHNICAL STUDIES

Janusz Chrzanowski
Akademia Morska w Szczecinie
Wydział Mechaniczny
ul. Wały Chrobrego 1-2
70-500 Szczecin
e-mail: j.chrzanowski@am.szczecin.pl
Bohdan Bieg
Wydział Mechaniczny
ul. Wały Chrobrego 1-2
70-500 Szczecin
e-mail: b.bieg@am.szczecin.pl

Abstract: The authors present the advantages and disadvantages of introducing quantum elements of metal physics into the curriculum of engineering studies. On the one hand, the rapid development of new technologies forces future engineers to acquaint with the foundations of quantum theory of metals, but on the other hand, these theories use complex mathematical formalism, which requires additional hours in the physics program. What is more, not all quantum theories lead to correct results. This paper presents the foundations of two quantum theories that lead directly to analytical equations: free electron theory and Hartree-Fock theory. Then, using the theoretical equations, we calculate the bulk modulus of the metals and compare the obtained results with experiment. Then we analyze the causes of discrepancies occurring in both theories.

Keywords: quantum elements of metal physics, free electron theory, Hartree-Fock theory.

Introduction

Discussions on the teaching of physics in technical colleges must essentially come down to search for answers to the question of how to educate the future engineer on the threshold of the twenty-first century. The development of such industries as materials' science, microelectronics and optoelectronics, is the result both of the modernization of existing and construction of new industrial plants using the latest technology. This of course creates a demand for engineering staff capable of following the development of science and technology, as well as creative activities in industry. In addition, due to the inevitable process of integration of our country into the European Union the problem of adequate education of engineering cadres in the field of physics, as well as personnel able to meet the new challenges posed by modern science and technology take on particular importance. There is a necessity to remember and remind constantly that the development of technical sciences and a number of others is closely linked with the achievements of physics. It is precisely understood physics which enables graduates to understand the new technologies and the right attitude to them.

Quantum physics science in school is certainly one of the most difficult challenges both for students and teachers [1]. The difficulty in understanding and teaching quantum physics, however, are a unique opportunity to show science as an integrated whole and a set of rules for carrying out accounts, which are often required in engineering and technology. All macroscopic properties and behavior of matter come directly from microscopic properties and behavior of the constituting particles, which can only be described with quantum physics. Therefore it is suggested that modern mechanical engineers must understand the fundamentals of quantum physics which is not understandable from everyday experience, moreover sometimes it even contradicts such experience [2]. But quantum physics is proved to be correct beyond reasonable doubt by an infinite number of experiments, and with time the validity of quantum physics was confirmed. The wide recognition of the relevance of quantum physics in current technologies, its role in science training and in the culture of science have enhanced research into new ways to present the subject in introductory physics courses. What is worse, the development of topical technologies is directly connected with physics of solids and thus the most sophisticated area of quantum physics. Thus the inclusion of applications of quantum mechanics to real although often simplified problems is not only important for the understanding of quantum physics, but will also motivate students to continue their studies in this subject [3]. On the other hand, one should keep in mind that attention paid only to mathematical

complexities makes loss to the real meaning of the phenomenon. Therefore, the problem of reducing more difficult concept into simpler terms becomes central to didactic reflection in quantum physics more than in any other topic.

Mathematical models in physics

In physics, the experimental results are given in the form of numbers and principles expressed mathematically. Mathematics is the language of physics therefore without the use of mathematics we are unable to describe physical phenomena [4]. Mathematics is an instrument in the research and is used to formulate mathematical models. When faced with a specific situation of physical physicist is trying to make its mathematical idealization or, as we say, simulation, preparing an idealized mathematical model of this situation, according to the following scheme in Fig. 1.

Traditionally, it is assumed that the mathematical model is a consistent system of mathematical equations

describing the analyzed phenomenon fulfilling the conditions laid down by Hadamard [5, 6]:
- a solution exists,
- the solution is unique,
- the solution's behavior changes continuously with the initial conditions.

In order to construct the model we need to distinguish certain measurable quantities typical for a given phenomenon that can be used for its verification. The fundamental theories according to which the model has been created should also be defined. The basic difficulty in formulating a proper model depends, on the one hand, on choosing the right one, that is measurable with physical parameters, and the other on the construction of understandable mathematical structures. In the case of physics of metals there are virtually only two models that comply with all the reservations above:
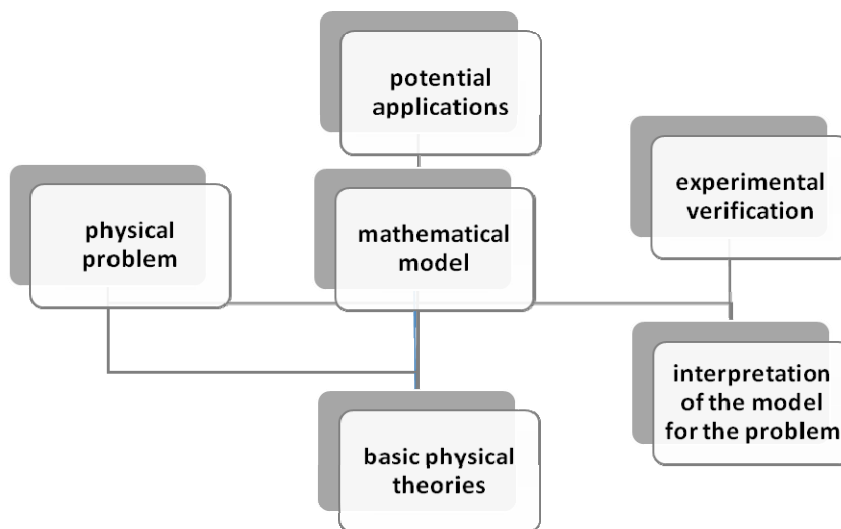- free electrons theory ,
- Hartree-Fock theory.

Fig. 1. Scheme of mathematical models.

The free electrons theory

A free electron model is the simplest way to represent the electronic structure of metals. The theory was proposed in 1900 to describe and correlate the electrical and thermal properties of metals. Although, the free electron model is a great oversimplification of the reality, surprisingly in many cases it works pretty well, so that it is able to describe many important properties of metals. According to this model, the valence electrons of the atoms become conduction electrons and can travel freely throughout the crystal. Therefore, within this model we can neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons. In this sense we are

talking about a free electron gas. However, there is a principle difference between the free electron gas and ordinary gas of molecules. Firstly, electrons are charged particles, so in order to maintain the charge neutrality of the whole crystal, we need to include positive ions. Secondly, the free electrons must comply with the Pauli exclusion principle, which leads to next important consequences.

In this case the Schrödinger equation takes an extremely simple form:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(r) = E\Psi(r) \,. \qquad (1)$$

It can be solved by elementary methods giving in result

$$\Psi(r) = \frac{1}{\sqrt{V}} e^{-ikr} \ . \tag{2}$$

and consequently the energy states of a single electron we obtain as:

$$E(k) = \frac{\hbar^2 k^2}{2m} \ . \tag{3}$$

Taking into account the Born-Karman boundary conditions:

$$\Psi(x + L, y, z) = \Psi(x, y, z)$$
$$\Psi(x, y + L, z) = \Psi(x, y, z) \tag{4}$$
$$\Psi(x, y, z + L) = \Psi(x, y, z)$$

we get that the components of the wave vector $\mathbf{k}$ must belong to the discrete set determined by equation:

$$k_i = \frac{2\pi n_i}{L}; n_i \in N; i \in \{x, y, z\} \ . \tag{5}$$

In practical terms quantization (5) is used primarily to determine the density of states in k-space. As a result directly from (2) volume per one allowed state in the space k is:

$$\bar{\omega} = \frac{(2\pi)^3}{L^3} \ . \tag{6}$$

Construction of N electron ground state comes down to filling the successive allowed states (3) with regard to the Pauli principle. Thus, for very large values of N region filled up by electrons in the $\mathbf{k}$-space will correspond to a sphere of radius k_F called the Fermi radius (Fig. 2). It is easy to show that:

$$k_F = \sqrt[S]{3\pi^2 n} \ . \tag{7}$$

where n means the electron density.

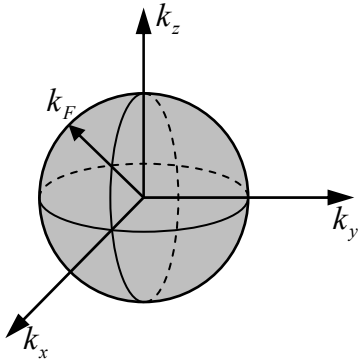Fig. 2. The Fermi radius k_F.

This means that the Fermi radius has a purely geometric interpretation, namely the radius of the sphere in the spatial space that separates the occupied states from the free ones. The free electrons theory created the basic concepts used in the physics of metals, such as the above-mentioned Fermi radius, the corresponding energy called Fermi energy, next temperature and Fermi sphere, whose appointment was for many years the main problem for any theory of metals. Moreover, the theory of free electrons can calculate the total energy of the N electrons ground state. For this purpose, we need to sum the energies of all single-electron levels lying inside the Fermi sphere:

$$E = 2 \sum_{k \le k_F} \frac{\hbar^2 k^2}{2m} \tag{8}$$

where factor 2 before the sum is the result of two spins per each value of k. By converting the sum into integral we get the energy density of the electron gas in form:

$$\in = \frac{E}{V} = \frac{\hbar^2 k_F^S}{10m\pi^2} \ . \tag{9}$$

Knowing the energy of the ground state, we can use all the thermodynamic relations and determine the pressure of the electron gas:

$$p = -\left(\frac{\partial E}{\partial V}\right)_N = -\in + n\frac{\partial \in}{\partial n} \tag{10}$$

as well as the bulk modulus defined as:

$$B = -V\frac{\partial p}{\partial V} = n^2 \frac{\partial^2 \in}{\partial n^2} \ . \tag{11}$$

Therefore having regard to relation (9) we obtain an equation allowing us to directly calculate the bulk modulus:

$$B = \frac{n^{5/3}\pi^{4/3}\hbar^2}{3^{1/3}m} \ . \tag{11a}$$

Of course, it can be assumed that these values will not always be precise, but any opportunity to connect the quantum world to the real one is always attractive for many reasons.

Hartree Fock theory

Hartree Fock [7] theory is one of the simplest approximate theories for solving the many-body Hamiltonian. It is based on a straightforward approximation to the true many-body wave function: that the wave function is given by a single Slater determinant of N spin-orbitals:

$$\Psi(r_1\sigma_1, r_2\sigma_3, ..., r_N\sigma_N) = \begin{bmatrix} \psi_1(r_1\sigma_1) & \psi_1(r_2\sigma_2) & ... & \psi_1(r_N\sigma_N) \\ \psi_2(r_1\sigma_1) & \psi_2(r_2\sigma_2) & ... & \psi_2(r_N\sigma_N) \\ . & . & ... & . \\ . & . & ... & . \\ . & . & ... & . \\ \psi_N(r_1\sigma_1) & \psi_N(r_2\sigma_2) & ... & \psi_N(r_N\sigma_N) \end{bmatrix} \ . \tag{12}$$

As long as we are content to consider molecules near their equilibrium geometry, Hartree-Fock theory often provides a good starting point for more elaborate theoretical methods which are better approximations to the electronic Schrödinger equation (e.g., many-body perturbation theory, single-reference configuration interaction).

It is always important to remember the context of a theory. Hartree-Fock theory was developed to solve the electronic Schrödinger equation that results from the time-independent Schrödinger equation after invoking the Born-Oppenheimer [7, 8] approximation. Again, the Hartree-Fock method seeks to approximately solve the electronic Schrödinger equation, and it assumes that the wave function can be approximated by a single Slater determinant made up of one spin orbital per electron. Since the energy expression is symmetric, the variational theorem holds, and so we know that the Slater determinant with the lowest energy is as close as we can get to the true wave function for the assumed functional form of a single Slater determinant. The Hartree-Fock method determines the set of spin orbitals which minimize the energy and give us this best single determinant.

The proper choice of the potential *V(r)* appearing in the one-electron Schrödinger equation is a subtle problem with basic question of how to represent the effects of electron-electron interactions best. From a fundamental point of view the Schrödinger equation should take into consideration both the electrons interactions

$$V_{el}(r) = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \psi \qquad (13)$$

and potentials of the ions

$$V_{ion}(r) = -Ze^2 \sum_R \frac{1}{|r - R|} \psi \quad . \qquad (14)$$

So as a consequence any calculation of the electronic properties of a metal should start with the Schrödinger equation for the N – particle wave function of all N electrons in the metal, including explicitly the dependence of wave function on the position, as well as the electron spin:

$$\hat{H}\psi = \sum_i^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 \psi - Ze^2 \sum_R \frac{1}{|r_i - R|} \psi \right) +$$
$$+ \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \psi = \hat{E}\psi \qquad (15)$$

Treating the remaining electrons as a smooth distribution of negative charge with charge density ρ, we can present the potential energy of the given electron in this field as:

$$V_{el}(r) = -e \int d^3r' \rho(r') \frac{1}{|r - r'|} \qquad (16)$$

what leads directly to the set of one-electron equations known as the Hartree equations for each occupied one – electron level:

$$-\frac{\hbar^2}{2m} \nabla_i^2 \psi_i(r) - Ze^2 \sum_R \frac{1}{|r - R|} \psi_i(r) +$$
$$+ \left[\sum_j \int d^3r' \frac{e^2}{|r - r'|} |\psi_j(r')|^2 \right] \psi_i(r) = E_i \psi_i(r) \qquad (17)$$

These nonlinear equations are solved by iteration until the procedure does not essentially change the potential. The antisymmetry requirement due to Pauli principle demands replacing the wave functions – solutions of equations (17) by a Slater determinant of one- electron wave functions. As a result we obtain set of Hartree-Fock equations:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{el}(r) + V_{ion}(r) \right) \psi_i(r) -$$
$$- \sum_j \int d^3r' \frac{e^2}{|r - r'|} \psi_j^*(r') \psi_i(r) \psi_j(r) \delta_{s_i s_j} = E_i \psi_i(r) \qquad (18)$$

here $\delta_{s_i s_j}$ results from including the dependence of wave function on the electron spin.

These equations differ from the Hartree equations (17) by an additional term:

$$-\sum_j \int d^3r' \frac{e^2}{|r - r'|} \psi_j^*(r') \psi_i(r) \psi_j(r) \delta_{s_i s_j} \qquad (19)$$

known as the exchange term. Like V_{el} (16) it is nonlinear in Ψ and what is worth emphasize it is not in the typical form *V(r)Ψ(r)* but has the structure of integral operator:

$$\int V(r, r') \Psi(r') d^3r' \qquad (20)$$

what made the Hartree-Fock equations difficult to solve except for the case of free electrons when they can be solved exactly by means of a set of orthonormal plane waves. Solution of the equations (18) leads to energy of an electron at the level *k* in the form:

$$E(k) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi} k_F \left[\frac{1}{2} + \frac{1 - \left(\frac{k}{k_F}\right)}{4\frac{k}{k_F}} \ln \left| \frac{1 + \frac{k}{k_F}}{1 - \frac{k}{k_F}} \right| \right] . \qquad (21)$$

As in the case of the free electron theory we can calculate the total energy of the *N* electrons ground state, so integrating eq. 21 we obtain:

$$\varepsilon = \frac{E}{V} = \int_0^{k_F} \frac{E(k)\pi k^2}{\pi^3} dk = \frac{k_F^4 (-5e^2 m + \pi \hbar^2 k_F)}{10m\pi^3} . \qquad (22)$$

Taking into account relation (7) we obtain:

$$\varepsilon = \frac{n^{4/3} 3^{4/3} (5e^2 m + 3^{1/3} n^{1/3} \pi^{5/3} \hbar^2)}{10m\pi^{1/3}} . \qquad (23)$$

This means that in this case the energy density like in TES is only function of the electron gas density *n*. Therefore, using the equation (11) we can express the bulk density *B* in form

$$B = -\frac{2e^2 n^{4/3}}{3^{2/3} \pi^{1/3}} + \frac{n^{5/3} \pi^{4/3} \hbar^2}{3^{1/3} m} . \qquad (24)$$

Calculation of the bulk modulus and comparison with experimental results

On the basis of equations (11a) and (24) we are able to calculate the bulk modulus for any metals. The results obtained directly from these equations for alkali metals are presented Fig. 3.

Apparently, for alkali metals, we observe high compatibility of experimental results with values derived directly from equations (11a) and (24). But according to H-F theory, the bulk modules obtained from equation (24) receive negative values for metals with electron gas density $n \langle 5,88 \cdot 10^{22}$ cm^{-3} – as alkali metals (Fig. 4). Therefore in the Fig. 5 the absolute values are shown.
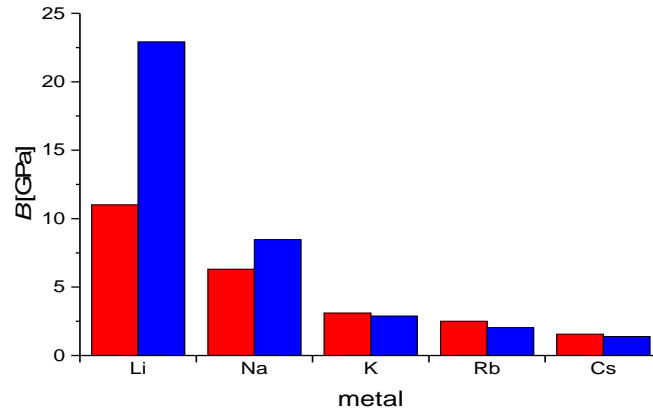
Fig. 3. Bulk modulus for alkali metals –comparison between experimental values (red) and free electrons theory values (blue), obtained from eq. (11a).
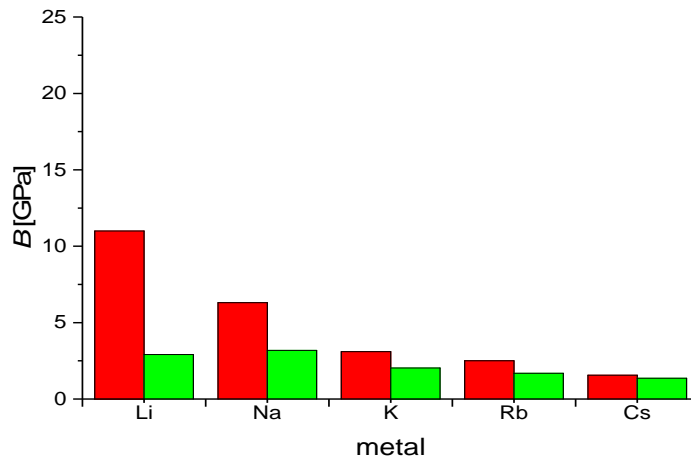

Fig. 4. Bulk modulus for alkali metals – comparison between experimental values (red) and H-F theory values (green), obtained from eq. (24).
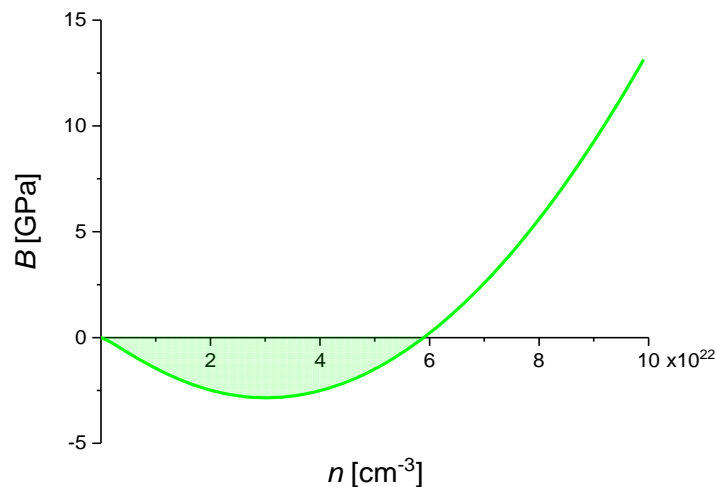

Fig. 5. Bulk modulus in dependence on electron gas density in terms of H-F theory, eq. (24).

This fact put the results of the H-F theory for this group of metals into justified doubt. There is, however, a significant group of metals for which one or the other theory leads to quite correct results. Figure 6 shows the metals for which the correct results give the theory of free electrons, while in graph 7 the theory of H-F. And, in contrast, Figures 8 and 9 show bulk modulus for metals where the difference between experimental and theoretical values is significant.
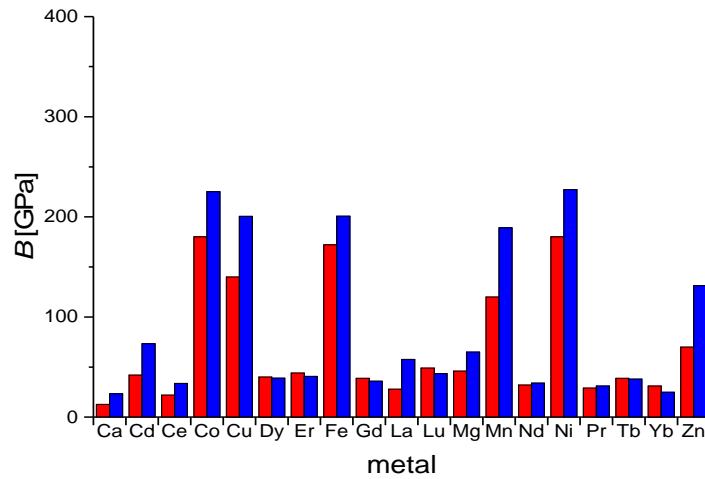

Fig. 6. Bulk modulus for the chosen metals –comparison between experimental values (red) and free electrons theory values (blue), obtained from eq. (11a).
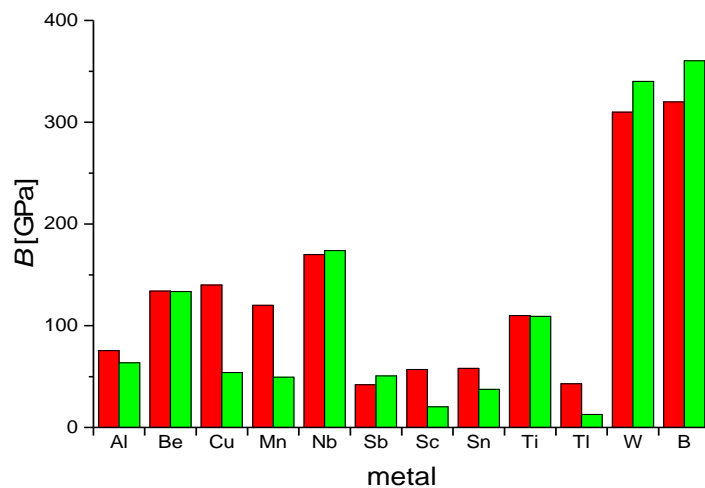

Fig. 7. Bulk modulus for the chosen metals – comparison between experimental values (red) and H-F theory values (green), obtained from eq. (24).
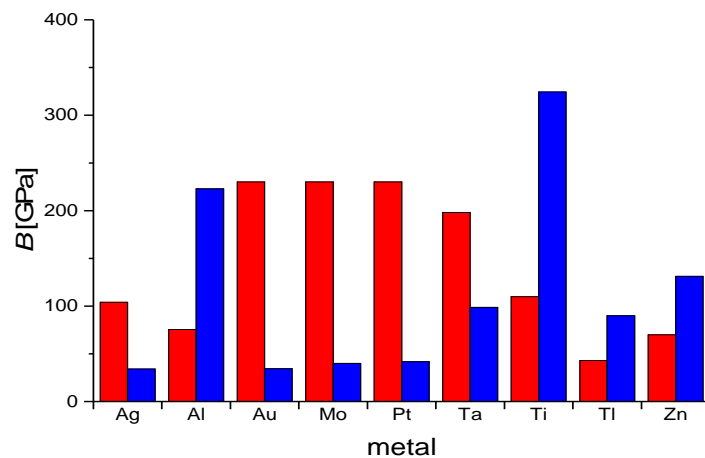

Fig. 8. Bulk modulus for the metals where the difference between experimental values (red) and free electrons theory values (blue) – obtained from eq. (11a), is significant.
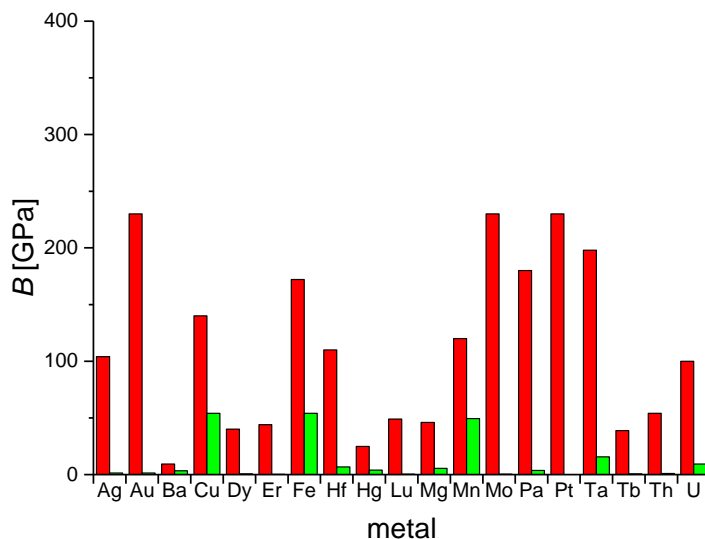
Fig. 9. Bulk modulus for metals where the difference between experimental values (red) and H-F theory values (green) – obtained from eq. (24) is significant.

Conclusions

The best correlation between theory and experimental results is observed for the alkali metals, obviously assuming absolute values for H-F theory. There are metals for which both theories give comparable results to the experiment (the differences do not exceed several percent), but in principle they are different metals for each theory, see Fig.5 and Fig.6. There are also metals for which the difference between theory and experiment is significant especially for noble metals where even the order of magnitude does not agree (Fig.7 and Fig.8). In this situation it is difficult to say that one of the theories gives a correct picture of the reality. It may seem strange that more correct results are obtained for a much simpler theory of free electrons, in which we do not formally take into account interactions. This means that the interaction, and especially the exchange energy (Eq. 19), may not be as significant as the H-F theory suggests.

All this puts into question the sense of the use of quantum models for practical calculations. If generally accepted course book models lead to substantial disproportions with the experiment the more difficult it becomes to present them in a reasonable way to students who are unfamiliar with complex physical formalism. This means that the current state of knowledge allows only for a qualitative analysis and this in turn significantly reduces the possibility of practical use.

References

1. Auletta, G., Foundations and Interpretation of Quantum Mechanics. World Scientific, London, 2000.
2. Treagust, D.F., Chittleborough, G., Mamiala, T.L., Students' understanding of the role of scientific models in learning science, *Int. J. Sci. Educ.*, 24, 357, 2002.
3. Greca, I.M., Moreira, M.A., Mental, physical, and mathematical models in the teaching and learning of physics, *Sci. Educ.*, 86, 106, 2002.
4. Gilbert, J.K., Models and modelling: routes to more authentic science education, *Int. J. Sci. Math. Educ.* 2, 2004.
5. Hadamard, J., Psychologia odkryć matematycznych, PWN, Warszawa, 1964.
6. Shaposhnikova, T.O., Hadamard, J.,: A Universal Mathematician, American Mathematical Soc., 1999.
7. Ashcroft, N.W., Mermin, N.D., Solid State Physics, Harcourt, Orlando, 1976.
8. Kittel, Ch., Introduction to Solid State Physics, Wiley, New York, 2004.