A semiempirical model for calculation of the energies of states of multielectron ions

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The methods of calculating the energy levels of multielectron, multiply charged ions based on a perfected model of the Bohr atom are reviewed. In addition to the electrostatic interaction, account is taken of the electrons in different orbits in the form of interaction of electric currents. The interaction constants for different electron configurations are chosen empirically. The calculated energy levels of He-, Li-, Be-, and B-like ions agree with the experimental values with a relative accuracy of 10^{-3} - 10^{-4} . An application of this method of calculation to atoms at constant volume is presented. A semiempirical equation of state of solids is derived, starting with a model of an isolated atomic cell. By using the experimental values of the bulk moduli, the effective energy of the unit atomic cell is calculated for more than 100 elements and compounds. Attention is called to the fact that different phases of solids differ not only in crystal structure, but also as a rule in the electronic states of the atoms.

INTRODUCTION

The quantum model of the atom created by N. Bohr in 1913 has played an extremely important role in the development of science. On the one hand, it summed up experimental and theoretical studies of atomic spectra of more than 50 years. On the other hand, it marked the beginning of the fundamental change of view of the microworld that culminated in the creation of wave quantum mechanics.

Spectral analysis as a method of studying materials was proposed and introduced into practice by R. Bunsen and G. Kirchhoff in 1859. I. Balmer in 1885 discovered the first laws in the spectrum of the hydrogen atom for the series of lines in the visible region of the spectrum. He showed that their wavelengths are described to high accuracy by a single formula operating with the squares of integers. Much material on the spectroscopy of atoms was obtained and generalized by Rydberg. The fundamental law in atomic spectroscopy, which was established empirically in 1908, is the combination principle of Ritz, according to which the whole variety of spectral lines of an atom can be obtained by pairwise combination of a far smaller number of quantities called the spectral terms. The view that energy can be transferred in discrete portions arose in explaining the laws of emission of an absolute black body (M. Planck, 1900). The quantum character of the emission was confirmed by study of the photoelectric effect and Compton scattering.

Important steps in the study of the properties of atoms were the planetary model of the atom and the proof by E. Rutherford based on experimental data on large-angle scattering of α -particles of the fact that the entire mass of an atom is concentrated at its center in the positively charged nucleus. A system consisting of a nucleus and an electron revolving around it is unstable from the standpoint of classical electrodynamics. Continuous emission of energy by the electron should cause it to fall into the nucleus, which does not actually happen. N. Bohr formulated postulates that remove this contradiction, and constructed the first quantum theory of the atom.^{1,2}

Bohr's theory of the hydrogen atom gave a graphic and extremely exact description of the energy levels of oneelectron ions. It allowed deriving the spectral laws discovered earlier (the Balmer series and others), to predict new spectral series, and to determine the Rydberg constant from known elementary constants. On its basis an understanding of the isotope shift of spectral lines was gained. The theory explained the Ritz combination principle, revealed the physical meaning of the spectral terms, which, as it turned out, are determined by the energy levels of the atom. A generalization of Bohr's theory to the case of elliptical orbits of electrons and an explanation of the fine splitting of spectral lines was given by A. Sommerfeld in 1916 (see Ref. 3).

Bohr's theory in its initial formulation^{1,2} was not restricted to the hydrogen atom and hydrogen-like ions. In Refs. 1 and 2 Bohr, moreover, studied models of states of the atoms of helium, lithium, beryllium, and proposed a model of the electronic structure of the molecule and the molecular ion of hydrogen, and drew a general picture of the structure of complex atoms. However, for complex atomic systems, it was not then possible to obtain the impressive agreement with the experimental data that was found for one-electron ions at the instant of creation of the theory, and which was subsequently confirmed.

The significance of Bohr's theory reaches far beyond the framework of calculating the wavelengths of spectral lines. It facilitated the development of physical concepts of atomic phenomena as a whole, and ultimately led to the creation of wave quantum mechanics. The de Broglie hypothesis, the matrix mechanics of Heisenberg, and the wave mechanics of Schrödinger were the basis of the new understanding of phenomena of the microworld. At the same time P. Dirac derived the relativistic equation, which takes account also of the spin of the electron.

Recently considerable attention has been paid to the

experimental and theoretical study of ions of high ionization multiplicity with a large nuclear charge Z. In this case one must take accurate account in the calculations of relativistic and radiation effects. The Schrödinger equation, being non-relativistic, requires taking account of relativistic effects in the form of corrections. For spectroscopic calculations of multiply charged ions the Dirac equation is more suitable. In both cases one must also take account of the radiation effects of quantum electrodynamics.

A rich literature exists on the quantum-mechanical methods of calculating atomic characteristics, both reflecting the general theoretical approach,^{4–8} and that devoted to concrete methods of calculating multielectron, multiply charged ions.^{9–14} There are also simplified methods.^{15,16} With the development of machine methods of numerical calculation, quantum-mechanical calculations have become accessible for rather complex multielectron systems (see, e.g., Refs. 17–19). As before, the empirical methods of calculation are of great practical importance.^{20–22}

At the same time the advances in exact quantummechanical calculations and the first failures of applying the Bohr model to multielectron atoms and ions favored the development of the opinion that the Bohr model was inapplicable to such systems. Moreover, the exact description by the Bohr theory of the spectra of the hydrogen atom is often considered to be fortuitous. However, recently one can note a certain interest in the semiclassical methods in atomic calculations. Thus, in Refs. 23–25 a calculation of the energy of the ground state of helium-like ions is performed by methods that are a modification of the Bohr model. Reference 26 gave a quasiclassical method of calculating the energy of states of helium-like and lithiumlike ions. There is also a classical model of the molecular ion of hydrogen.²⁷

The classical views of the motion of atomic electrons are successfully used to calculate the cross sections of interaction of fast electrons with atoms. An example might be the Thomson formula,²⁸ which was derived as early as the prequantum epoch, and its more contemporary modifications.²⁹⁻³¹ In numerical calculations of the ionization of the hydrogen atom by electrons,³² in which the classical three-body problem was solved, good agreement with the experimental data was obtained. The classical and quasiclassical approaches to problems involving the Stark and Zeeman effects have been discussed in detail in the review, Ref. 33, which concluded that the potentialities of the classical methods in atomic calculations are far from exhausted.

Below we review the methods of calculating the energy of the states of multielectron, multiply charged ions based on a refined model of the Bohr atom. Perhaps the use of the Bohr model to solve these problems is reflected in the literature to the least extent. It turns out that, by these methods within the framework of a unitary approach, one can study the energy of free atoms and ions (for which an infinite volume is accessible),^{34–36} the energy of states under conditions of restricted volume (e.g., for atoms contained in a solid),^{37–39} and also the electronic energy levels of molecules.⁴⁰ Thus one can obtain a number of new results.

The approach being applied is based on development of the ideas of N. Bohr involving the description of an atom on the basis of planetary orbits in combination with the corresponding quantization rules. The basis of the quantization is the quantization (integer values in units of h) of the angular momentum of the electrons. In this case the energy proves to be a multiparameter function of the coordinates corresponding to the different atomic shells. The quantization (discreteness) of the energy is obtained as a consequence of the quantization of the angular momentum. Perhaps this viewpoint on the quantization of the energy was most clearly formulated in Ref. 41.

A sufficiently exact calculation of the energy of multielectron atoms and ions proves possible only with a semiempirical approach. As compared with the study of N. Bohr,^{1,2} in calculating multielectron atoms, in addition to the electrostatic Coulomb interaction, one takes account of the additional interaction of the electrons in the form of the interaction of electric currents.³⁴⁻³⁶ The constants of this additional interaction are chosen empirically. While leaving unaltered the integer values of the quantization of the angular momentum, this approach shifts the difficulties into the region of describing the interaction of the atomic particles. One can say that, while the Bohr theory of the hydrogen atom postulated the inapplicability of classical electrodynamics to processes of emission of energy from the atom (while leaving the Coulomb interaction unchanged), then for multielectron atoms, in addition, one must use the interaction of the electric currents in the atom with a constant differing from that obtained in classical electrodynamics.

In the model one uses only circular orbits of electrons. However, this does not mean that one ignores in the calculations the dependence of the energy on the orbital quantum number. The magnitudes of the empirical parameters depend on it, just as on the spin. The quality of the semiempirical method is determined by the number of empirical constants that are employed. In the model being discussed, for each type of states with given L and S, one uses two empirical constants that do not depend on Z, n, and j, and which allow one to obtain a large bulk of calculated values for ions having different nuclear charges Z in different excited states. In contrast to a number of simplified classical and quasiclassical calculations that operate with only one type of state, $^{23-25}$ or those that do not distinguish states with a different value of the spin,²⁶ the semiempirical method presented below enables one to calculate the energy of states of rather complex multiply charged ions with an accuracy sufficient for comparison with spectroscopic data. The comparison of the calculated quantities in the review is conducted both with the experimental data and, as much as possible, with the results of the most contemporary exact quantum-mechanical calculations. The calculations of the energy are relativistic, which enables obtaining results and making a comparison for ions with large nuclear charges Z.

The question might arise: what is the sense of such

semiempirical calculations when there is a developed, more exact theory? The merit of the model being discussed, just as of the Bohr model in its time, is the simplicity and graphic character of the physical concepts used and the minimal bulk of necessary calculations. In a number of cases one can obtain analytic expressions for the energy of states, in particular for the energy of the ground state of helium-like ions, taking account of relativistic effects and applicable to ions of large Z,³⁶ and analytic expressions for the energy of highly excited Rydberg states of helium-like and lithium-like ions.³⁴

The method of energy calculation developed for atoms and atomic ions has proved applicable to calculating the energy of excited electronic states of molecules.⁴⁰ Upon using the same electronic configuration for the hydrogen molecule as for the helium atom, one can obtain by calculation the energy levels of the H_2 molecule in one-electron excited states and establish their correspondence to the experimental values. The contrast with the helium atom is manifested in the fact that the electrons lie in the field of two nuclei with Z=1 separated by a certain distance, rather than a single point charge with Z=2. This appreciably increases the radius of the orbit of the inner electron and causes a certain change in the energy of interaction of the outer with the inner electron, while the values of the empirical constants of the additional interaction with respect to the helium atom remain the same.

Another rather successful application of the method being used is the study of strongly compressed matter. By this method one can rather simply study the energy states of an atom under conditions of restricted finite volume per atom, and view the compression of a solid as the compression of an electrically neutral cell containing one or several atoms. Here the pressure in the solid that arises upon compression is determined by the radius of the outer electron shell. From the condition of quantization of the angular momentum, the energy of a multielectron atom is represented by a multiparameter function of the coordinates. The stationary states of the free atoms are determined by minimizing this function. In the compressed atom the value of the energy corresponds to a concrete value of the radius of the outer electron shell and does not equal the minimum value. Thus, one is studying nonequilibrium states in the compressed atom. Here the energy of the atom varies smoothly and continuously in the process of compression with a fixed quantum state. This is another difference of the method of calculation being applied as compared with the original formulation of the model of N. Bohr, which treated only equilibrium states corresponding to minimum energy.

Atoms occupying a restricted volume attract the attention of researchers as a model for estimating the influence of the environment on the properties of atoms in real objects.^{42,43} Particles are studied inside an impenetrable spherical cavity. Under such conditions the energies have been calculated of atomic hydrogen,⁴² atoms of He, Li, Be, B, C, and Ne,⁴³ and of two-electron ions (H^-, He, Li^+) .⁴² One of the methods of studying such systems adopted in Ref. 42 is the quantum Monte Carlo method,^{44,45} while also the Hartree–Fock method is used.⁴³ Upon decreasing the dimensions of the cavity the energy of the atomic state sharply increases. In the model of the Bohr atom this is explained by the increase in the kinetic energy upon decreasing the radius of the orbit of the electron with invariant angular momentum. Interesting comments on the influence of a finite volume on the states of atoms are found in the book, Ref. 46.

In the Bohr model approximate analytic expressions could be obtained for the elastic energy and the pressure. which can be used as a semiempirical equation of state of solids with the parameters E_n (energy of the outer electrons of the atomic cell) and ρ_n (density) under equilibrium conditions.^{37,38} It proved possible to write the elastic pressure, both in terms of the macroscopic quantity B_0 (bulk compression modulus) and in terms of the microscopic quantity E_n (effective energy of the cell). This enabled determining the effective energy of state of the atomic cell contained in a solid for a known value of the bulk compression modulus for many elements and compounds and to establish that the different phases of solids differ not only in crystal structure, but as a rule also in differing electronic state of the atoms (differing effective energy of the atomic cell of the solid).³⁹

The equation of state obtained in this way supplements the existing methods of calculation. A knowledge of the equation of state of substances is required in different fields of study. The range of variation of the parameters is very large, and each field has its own experimental and theoretical methods. Compression of solids at high pressure is studied both in static and in dynamic experiments. There is no opportunity in this review to reflect in any detail the experimental and theoretical studies on equations of state in different ranges of the parameters. It is devoted to different applications of the atomic model of Bohr, in particular to calculating the compressibility of substances. Therefore in the text the data on the equation of state (both experimental and calculated) are used mainly for comparison with the results obtained by the Bohr model. Since a large number of special reviews and monographs exists on the equation of state, $^{47-70}$ we shall briefly take up some of them and refer the reader to the literature contained in them.

The static studies, which were broadly conducted by P. Bridgman in the pressure region up to 10 GPa,⁴⁷ subsequently with the discovery of the technique of diamond anvils [see the review⁴⁸] were extended in pressure. Studies are already being conducted at pressures of 250 GPa,⁴⁹ 400 GPa,⁵⁰ and there is a prospect of obtaining a pressure of 1000 GPa.⁵⁰ Even higher pressure values are reached in shock-wave experiments.^{51–62}

The results of measuring the static compressibility of a large number of substances (to a considerable extent from the data of P. Bridgman) are given in the handbook, Ref. 63. The x-ray structural studies of compressed substances are very important.⁶⁴ The various features of the behavior of condensed substances and plasmas under dynamic shock-wave exposure are reflected in Refs. 51–62. A book has been recently published⁶¹ in which the studies of com-

pression of substances by shock waves are collected, mainly conducted by L. V. Al'tshuler and his students. A comparative analysis of the different thermodynamic models of the equations of state and a discussion of their limits of applicability over a broad range of parameters is given in the review, Ref. 57. References are presented in the same place to the published studies on this topic. Theoretical models of the equation of state are reflected in Refs. 65–75. Considerable attention has been paid to the study of the influence of the electron shells of atoms on the compressibility of substances at ultrahigh pressures.^{62,70–75}

Many studies have been devoted to investigating phase transitions in substances in shock waves and the features of the shock Hugoniots D(u) associated with these transitions.^{51-53,76-83} The model of the Bohr atom allows one quantitatively to determine the parameters of the electronic phases of solids and to conduct an analysis of the course of the D(u) curves for many elements and compounds, starting with the hypothesis that the different regions of the D(u) curve can correspond to different phases of the solid having a different equilibrium density and bulk compression modulus.⁸⁴

This review does not discuss the problems of the history of development of the theory of the Bohr atom (on this topic see Refs. 85–90). Its aim is to try to show the Bohr model, not as a historical phenomenon, but as an acting physical theory.

1. ENERGY LEVELS OF FREE ATOMS AND IONS

1.1. Hydrogen-like ions

As we know, the energy values of hydrogen-like ions are described by the Dirac-Sommerfeld formula^{3,6}

$$E(n,k) = mc^{2} \left[\left\{ 1 + \left[\frac{\alpha Z}{n - k + (k^{2} - \alpha^{2} Z^{2})^{1/2}} \right]^{2} \right]^{-1/2} - 1 \right], \quad (1)$$

where *n* is the principal quantum number, k=j+(1/2), *j* is the quantum number of the total angular momentum (the sum of the orbital angular momentum and the spin), α is the fine-structure constant, *m* is the mass of an electron, *c* is the speed of light, and *Z* is the nuclear charge of the ion. When k=n we have

$$E = mc^{2} \{ [1 - (\alpha^{2} Z^{2}/n^{2})]^{1/2} - 1 \}.$$
(2)

Let us present the derivation of Eq. (2) as the result of solving the relativistic problem in the Bohr-Sommerfeld model for circular orbits. Upon taking account of the motion of the nucleus, the value of the energy equals

$$E = mc^{2} \{ [1 - (v^{2}/c^{2})]^{-1/2} - 1 \} + (Mv^{2}/2) - (Ze^{2}/r).$$
(3)

Here *M* and *V* are the mass and the velocity of the nucleus, *e* is the charge of the electron, and *r* is the radius of its orbit. From the condition of quantization of the angular momentum of the electron $mvr[1-(v^2/c^2)]^{-1/2} = n\hbar$ we obtain

$$[1-(v^2/c^2)]^{-1/2}=[1+(\alpha^2n^2/x^2)]^{1/2}$$

where $x=r/a_0$; a_0 is the Bohr radius. Here the energy equals (in atomic units)

$$E(x) = \frac{1 + (m/M)}{\alpha^2} \{ [1 + (\alpha^2 n^2 / x^2)]^{1/2} - 1 \} - (Z/x),$$
(4)

while $\partial E/\partial x = 0$. From this we obtain the radius of the steady-state orbit

$$x = \frac{n^2 [1 + (m/M)]}{Z} \left[1 - \frac{\alpha^2 Z^2}{[1 + (m/M)]^2 n^2} \right]^{1/2}$$
(5)

and the energy value

$$E = \frac{1 + (m/M)}{\alpha^2} \left[\left\{ 1 - \frac{\alpha^2 Z^2}{\left[1 + (m/M) \right]^2 n^2} \right\}^{1/2} - 1 \right].$$
 (6)

When $m/M \leq 1$, Eq. (6) coincides with Eq. (2), and the atomic unit of energy is $\alpha^2 mc^2$. The velocity of the electron in motion in the orbit is the same as in the nonrelativistic case: $v = Z\alpha c/n$. We obtain from Eq. (5)

$$Z = \frac{n^2 [1 + (m/M)]}{x [1 + (\alpha^2 n^2 / x^2)]^{1/2}}.$$
 (7)

Substituting (7) into (4), we obtain

$$E = \frac{1 + (m/M)}{\alpha^2} \left\{ \frac{1}{[1 + \alpha^2 n^2 / x^2]^{1/2}} - 1 \right\}.$$
 (8)

Equation (6) contains no dependence on the magnitude of the total angular momentum j that exists in the Dirac theory. Upon substituting into the Dirac formula (1) the value of Z from (7), we obtain the energy for different values of j expressed in terms of the radius of the orbit of the electron. The difference between this value and Eq. (8) determines the multiplet shift of the energy levels $E_{\rm M} = D(x,n,j)$:

$$= \frac{1}{\alpha^{2}} \left(\left[1 + \left\{ \frac{\alpha \Phi(x,n)}{n - k + \left[k^{2} - (\alpha^{2} \Phi^{2}(x,n)) \right]^{1/2}} \right]^{2} \right]^{-1/2} - \frac{x \Phi(x,n)}{n^{2}} \right).$$
(9)

Here we have k=j+(1/2), while the function $\Phi(x,n)$ equals $n^2/(x^2+\alpha^2n^2)^{1/2}$.

The transition that has been made to a dependence of the energy on the radius of the orbit of the electron, rather than on the nuclear charge Z, naturally offers nothing new for hydrogen-like ions. However, it proves convenient in calculating atomic systems with a number of electrons greater than unity. The multiplet splitting known under the name of the fine structure of levels was first explained theoretically by A. Sommerfeld in 1916, starting with the concept of elliptical orbits, whereas we shall conduct the entire treatment for circular orbits, while introducing the correction (9) for the multiplet splitting.

Beginning at Z=10, the deviation of the experimental values from the values obtained by Eq. (1) becomes appreciable, in connection with the influence of radiation ef-

fects. The refinement of the calculated values of the energy of hydrogen-like ions in recent years has involved the perfection of the methods of calculating them.⁹¹⁻⁹⁴ On the basis of the data of Ref. 91, Erickson calculated detailed tables of the energy levels of one-electron ions with nuclear charges Z=1-105.⁹³ The measurements of the Lamb shift of the levels of hydrogen-like ions of phosphorus,⁹⁵ chlorine,⁹⁶ argon,⁹⁷ and nickel⁹⁸ show a closer coincidence with the results of the calculations of Mohr^{92,94} and are confirmed by the results of Johnson and Soff.⁹⁹ The magnitude of the Lamb shift is elevated in the calculations of Ref. 93.

Let us present the interpolation dependence for the radiation correction for s states $\Delta E_{rad} = L(x,n)$:

$$L(x,n) = \frac{3.375\alpha^3 n(n/x)^4}{1 + (0.114n^2/x)} - 0.0637\alpha^3 (n/x)^4, \quad (10)$$

where x is given by Eq. (5). The values of the radiation energy shift calculated by Eq. (10) of 1s states differ for Z < 70 from the data of Refs. 94, 99 by no more than 0.06 eV. The experimental values of the Lamb shift of the states $2s^2S_{1/2}$ and $2p^2P_{1/2}$ for the elements with Z=15, 17, and 18 are described by Eq. (10) to an accuracy of 2%.

1.2. Ground state of helium-like ions

According to Bohr the ground state of helium-like ions is described by a system of two electrons revolving in a single circular orbit (and with identical velocities) about the nucleus. Upon taking account of the quantization condition $mvr[1-(v^2/c^2)]^{-1/2} = \hbar$, the energy of the ground state equals

$$E(x) = \frac{2}{\alpha^2} \left\{ \left[1 + (\alpha^2/x^2) \right]^{1/2} - 1 \right\} - (2Z/x) + (1/2x).$$
(11)

In this model the center of gravity of the three particles (the nucleus and the two electrons) coincides with the nucleus, and the energy does not depend on the mass of the isotope. From the condition $\partial E/\partial x=0$, the radius of the steady-state orbit is

$$x = \frac{[1-\alpha^2(Z-0.25)^2]^{1/2}}{Z-0.25}.$$

The energy of the ground state of helium-like ions equals (in atomic units):

$$E(Z) = \frac{2}{\alpha^2} \{ [1 - \alpha^2 (Z - 0.25)^2]^{1/2} - 1 \}.$$
 (12)

The ionization potential of such ions equals the difference between the energy of (12) and the energy of the hydrogen-like ions. The ionization potential of the helium atom obtained in this calculational scheme by N. Bohr¹ amounts to 28.9 eV in place of the experimental value 24.59 eV.¹⁰⁰ With increasing Z the relative error of the calculated ionization potential declines. The difference between the calculated and experimental values of the ionization potentials depends linearly on Z:

$$I_{\rm calc} - I_{\rm exp} = (Z - 0.75)/8.$$

This dependence can be obtained by introducing into the calculation an additional interaction between the electrons in the form A/2x, besides the electrostatic Coulomb interaction. By comparison with the experimental data we have A=0.25. One can understand the 1/x functional dependence on the basis of the analogy with a ring electric current.

Let us turn attention to the fact that one can find the linear dependence that we have presented only for a relativistic formulation of the kinetic energy of the electrons. A nonrelativistic calculation yields a curve with a maximum at Z=14 for the difference between the experimental and calculated energies of the ground state of helium-like ions.

Often one uses the concept of screening of the charge of the nucleus by interaction of the electrons with one another. Owing to the Coulomb interaction of the electrons in helium-like ions, the screening coefficient (according to Bohr) equals $\sigma_{\rm B}=0.25$, the additional interaction gives $\Delta\sigma$ =0.0625, and the total screening coefficient is σ =0.3125. With account taken of this correction, the energy of the ground state of helium-like ions equals

$$E(Z) = 2mc^{2} \{ [1 - \alpha^{2} (Z - 0.3125)^{2}]^{1/2} - 1 \} - K.$$
(13)

Here K=1.52 eV is a constant term. When $\alpha Z < 1$, Eq. (13) is converted into the well known expression (see, e.g., Ref. 5)

$$E(Z) = -\alpha^2 m c^2 (Z - 0.3125)^2 - K.$$
(14)

Thus Eq. (13) is a natural generalization of Eq. (14) to the relativistic case. The correction for the relativistic dependence of the mass of the electron on the velocity equals

$$E_{\rm rel} = mc^2 [2\{[1-\alpha^2(Z-0.3125)^2]^{1/2}-1\} + \alpha^2(Z-0.3125)^2].$$
(15)

For large Z, as in the case of hydrogen-like ions, one must take account of radiation effects. The calculation of the radiation effects is a difficult independent problem. They were taken into account effectively in Ref. 36 by using a functional dependence, as for the hydrogen-like ions [i.e., in the form of (10)], and by choosing the coefficient so as to obtain the best calculated description of the existing experimental values. Starting with this, the following expression was taken for the radiation correction to the energy of the ground state of helium-like ions:

$$E_{\rm rad} = 2.828 L(x,n),$$
 (16)

where we have

L(x,n) from (10), and

$$x = [1 - \alpha^2 (Z - 0.3125)^2]^{1/2} / (Z - 0.3125)$$

The energy of the ground state of helium-like ions is the sum of the values obtained by Eqs. (13) and (16). The energy values of the ionization potentials calculated in this way for ions with Z=1-90 are given in Ref. 36. The difference between the calculated energy values and the experimental data¹⁰⁰ (for Z < 20) does not exceed 0.03 eV (relative accuracy 10^{-4} - 10^{-6}). We note that when Z=20 the relativistic correction of (15) amounts to 55 eV, and the radiation correction of (16) to 4.5 eV. The high accuracy of coincidence of the calculated and experimental values allows one to use with a high degree of reliance the calculated values for large Z, when there are no reliable experimental data. The calculated values¹⁹ of the ionization potentials of the ground state of helium-like ions describe the experimental results somewhat more poorly. but their difference from the data³⁶ for Z < 45 does not exceed 1.5 eV (relative error less than 10^{-4}).

1.3. Lithium-like ions

The formation of the ground state of lithium-like ions and their states with an excited outer electron can be represented as the combination of a helium-like ion in the ground state with an electron having the angular momentum $n\hbar$ (*n* is the principal quantum number of the outer electron). The energy of such systems includes the energy of the helium-like ion

$$\frac{2}{\alpha^2} \{ [1 + (\alpha^2/x^2)]^{1/2} - 1 \} - [2(Z - 0.3125)/x] - K,$$
(17)

the kinetic energy of the outer electron

$$\frac{1}{\alpha^2} \{ [1 + (\alpha^2 n^2 / y^2)]^{1/2} - 1 \},$$
(18)

and the energy of the electrostatic interaction of the outer electron with the inner ion

$$-(Z-2)/y.$$
 (19)

Here $x = r_1/a_0$, $y = r_2/a_0$, where r_1 and r_2 are the radii of the inner and outer orbits, and a_0 is the Bohr radius, with the energy in atomic units. The expressions for the energy are written with account taken of the quantization of the angular momentum of the electrons:

$$mvr_1[1-(v_1^2/c^2)]^{-1/2}=\hbar,$$

 $mvr_2[1-(v_2^2/c^2)]^{-1/2}=n\hbar.$

To find the correction to the interaction energy of the outer with the inner electrons, as in the ground state of the helium atom, we shall use the analogy with the interaction of electric currents. The energy of this interaction will be positive or negative, depending on the direction of motion of the electrons in the interacting rings (in the same or in opposite directions). The interaction energy of the currents equals¹⁰¹

$$E_{\rm int} \sim i_1 i_2 \int \frac{\mathrm{d}s_1 \mathrm{d}s_2}{r_{12}}$$
 (20)

For coaxial rings with a current radius of x and y we have

$$E_{\rm int} \sim i_1 i_2 \int_0^{2\pi} (x^2 + y^2 - 2xy \cos \varphi)^{-1/2} \mathrm{d}\varphi.$$
 (21)

The electric current is

$$i_{1,2} \sim ev_{1,2} [1 - (v_{1,2}^2/c^2)]^{1/2}.$$

Upon expressing $v_{1,2}$ in terms of x and y from the quantization conditions, we obtain: $i_1 \sim e\alpha c/x$, $i_2 \sim e\alpha cn/y$. As a result we can write the interaction energy in the form

$$E_{\rm int} = -2AnF(x,y), \qquad (22)$$

where we have

$$F(x,y) = -\frac{1}{2\pi} \int_0^{2\pi} \frac{\cos\varphi d\varphi}{(x^2 + y^2 - 2xy\cos\varphi)^{1/2}}.$$
 (23)

Here A is a constant determined by comparison with the experimental data. For a more complete agreement of the calculated values with experiment (especially for small Z), we shall take account in the energy of another correction term

$$-2Bx/ny,$$
 (24)

where B is an empirical constant. This correction amounts in order of magnitude to 0.5-1.0 eV, and is constant for large Z (being equal to B/n^3). The stationary states are determined from the conditions of energy minimum:

$$\partial E/\partial x = 0, \quad \partial E/\partial y = 0.$$

From these conditions we obtain the following equations

$$-\frac{1}{x^{3}[1+(\alpha^{2}/x^{2})]^{1/2}}+\frac{Z-0.3125}{x^{2}}-\frac{B}{ny}+AnF_{1}(x,y)$$

=0, (25)

$$-\frac{n^2}{y^3 [1 + (\alpha^2 n^2 / y^2)]^{1/2}} + \frac{Z - 2}{y^2} + \frac{2Bx}{ny^2} + 2AnF_2(x, y)$$

=0, (26)

where we have

$$F_1(x,y) = -\partial F(x,y)/\partial x$$

= $\frac{1}{2\pi} \int_0^{2\pi} \frac{(x-y\cos\varphi)\cos\varphi d\varphi}{(x^2+y^2-2xy\cos\varphi)^{1/2}},$ (27)

$$F_{2}(x,y) = -\partial F(x,y) / \partial y$$

= $\frac{1}{2\pi} \int_{0}^{2\pi} \frac{(y - x \cos \varphi) \cos \varphi d\varphi}{(x^{2} + y^{2} - 2xy \cos \varphi)^{1/2}}.$ (28)

After simple transformations we find that the energy of the stationary states equals

$$E(x,y) = \frac{2}{\alpha^2} \left[\frac{1}{1 + (\alpha^2/x^2)^{1/2}} - 1 \right] + \frac{1}{\alpha^2} \left\{ \frac{1}{\left[1 + (\alpha^2 n^2/y^2)\right]^{1/2}} - 1 \right\} - \frac{2Bx}{ny}.$$
 (29)

Thus the problem of determining the energy levels is reduced to finding x and y by solving the system of equations (25) and (26). This system can be solved by a simple iteration method. We note that, when x < y, we have

$$F(x,y) = \frac{1}{2\pi} \int_0^{2\pi} \frac{\cos \varphi d\varphi}{(x^2 + y^2 - 2xy \cos \varphi)^{1/2}}$$

TABLE I. Parameters of the 1s²nl states of lithium-like ions

| State | A | В |
|--------------------|----------|-----------|
| 1s ² ns | 0,8045 | 0,150 |
| 1s ² np | 0,2455 | - 0,084 |
| 1s ² nd | 0,0105 | - 0,003 |
| 1s ² nf | 0,0012 | - 0,00027 |
| 1s ² ng | 0,000169 | 0 |
| ls ² nh | 0,00005 | 0 |

$$=\sum_{n=0}^{\infty}\frac{x^n}{y^{n+1}}\frac{1}{\pi}\int_0^{\pi}\cos\varphi\cdot P_n(\cos\varphi)\,\mathrm{d}\varphi,\quad(30)$$

where $P_n(\cos \varphi)$ is the Legendre function. Using the expansion considerably accelerates the numerical calculation.

The calculated description of the energy of the $1s^2nl$ states of lithium-like ions is attained with the values of the parameters A and B given in Table I. These two parameters are chosen for each type of states of atoms having the given value of l, while not depending on Z, n, nor j. The relative accuracy of description of the energy is $10^{-3}-10^{-4}$.³⁵ For large Z one must take account of the shift of the energy levels as a function of the total angular momentum j. It proved possible to calculate this shift analogously to the calculation for hydrogen-like ions by starting with the expression

$$\Delta E_{\rm M} = D(y, n, j), \tag{31}$$

where D(y,n,j) is the function of Eq. (9). The values of y are determined by solving the system of equations (25) and (26). In the case in which the interaction of (22) and (24) is absent, Eq. (31) yields a value of the shift of levels coinciding with that in the Dirac theory for hydrogen-like ions with $Z^* = Z - 2$. Thus, upon using the values of the radii of the orbits of the electrons from solving the system (25) and (26), the energy of each electron is described by the Dirac formula written as a function of the radius of the orbit of the electron.

In calculating the energy of $1s^2ns$ states the following correction term was taken into account:

$$\Delta E = -L(y,n), \tag{32}$$

where L(y,n) is taken in the form of (10), which interpolates the Lamb shift of the *n*s states of the hydrogen-like ions. Moreover, another correction was used for the $1s^2ns$ states:

$$\Delta E = \frac{0.48\alpha}{y^2} \left(\frac{n}{2} - 1\right),\tag{33}$$

and for the $1s^2np$ states:

$$\Delta E = -\frac{0.68\alpha}{y^2} \left(\frac{n}{2} - 1\right). \tag{34}$$

When j=n-(1/2) the multiplet shift equals zero, and hence, for the states $2p {}^{2}P_{3/2}$, $3d {}^{2}D_{5/2}$, $4f {}^{2}F_{7/2}$, and $5g {}^{2}G_{9/2}$ the relativistic effects are fully taken into account in the relativistic form of writing the kinetic energy. In agreement with Eq. (31) the doublet splitting equals

TABLE II. Comparison of the calculated values of Refs. 35, 19, 102, and 103 of the ionization potentials of the ground state of lithium-like ions with the experimental data from Ref. 100.

| Z | 7 [100] | 1 [35] | 7 [19] | 1 [102] | 1 [103] |
|----|----------|----------|----------|----------|----------|
| 3 | 5,3918 | 5,4401 | _ | 5,3900 | 5,3917 |
| 4 | 18,2113 | 18,2041 | _ | 18,2098 | 18,2112 |
| 5 | 37,9309 | 37,9038 | — | 37,9300 | 37,9304 |
| 6 | 64,4944 | 64,4636 | 64,4951 | 64,4947 | 64,4939 |
| 7 | 97,8909 | 97,8637 | 97,8940 | 97,8928 | 97,8902 |
| 8 | 138,1205 | 138,1010 | 138,1241 | 138,1242 | 138,1194 |
| 9 | 185,1879 | 138,1787 | 185,1912 | 185,1947 | 185,1866 |
| 10 | 239,1007 | 239,1040 | 239,1037 | 239,1113 | 239,0990 |
| 11 | 299,8830 | 299,8865 | 299,8716 | 299,8858 | 299,8679 |
| 12 | 367,5417 | 367,5377 | 367,5069 | _ | 367,5034 |
| 13 | 442,0816 | 442,0710 | 442,0229 | 442,0553 | 442,0202 |
| 14 | 523,5151 | 523,5014 | 523,4345 | - | 523,4321 |
| 15 | 611,8670 | 611,8453 | 611,7585 | 611,8187 | 611,7567 |
| 16 | 707,1620 | 707,1209 | 707,0127 | _ | 707,0102 |
| 17 | 809,4126 | 809,3478 | 809,2164 | 809,3162 | 809,2133 |
| 18 | | 918,5472 | 918,3907 | — | 918,3865 |
| 19 | _ | 1034,742 | 1034,558 | | 1034,549 |
| 20 | _ | 1157,955 | 1157,743 | 1157,931 | 1157,727 |
| 22 | — | 1425,545 | 1425,267 | 1425,539 | |
| 24 | — | 1721,541 | 1721,186 | 1721,563 | — |
| 26 | — | 2046,196 | 2045,749 | 2046,259 | _ |
| 28 | | 2399,785 | 2399,233 | 2399,906 | _ |
| 30 | — | 2782,617 | 2781,939 | 2782,813 | |
| 33 | — | 3412,430 | 3411,527 | 3412,781 | |
| 36 | | 4110,054 | 4108,870 | 4110,616 | - |
| 41 | — | 5427,389 | 5425,581 | 5428,471 | |
| 54 | — | 9812,675 | | 9816,698 | — |

$$\Delta E({}^{2}L_{l+(1/2)} - {}^{2}L_{l-(1/2)})$$

= $D(y,n,l+(1/2)) - D(y,n,l-(1/2)).$ (35)

Table II compares the calculated ionization potentials of the ground state of lithium-like ions obtained by this method with the experimental data¹⁰⁰ and with the results of other calculations.^{19,102,103} The calculated values³⁵ describe the data of Ref. 100 for ions with Z=3-17 to an accuracy better than 0.03–0.06 eV. For Z=18-20 the tables of Ref. 100 give approximate estimated values. Isoelectronic extrapolation of the ionization potentials by the method of Ref. 104 yields values for the ion ArXVI of 918.61±0.01 eV, for the ion KXVII of 1034.81±0.04 eV, and for the ion CaXVIII of 1157.97±0.02 eV, which differ little from the values in Ref. 35. This same table presents the calculated values of Ref. 102, which are close to the calculated quantities of Ref. 35 for the ions with Z up to 25.

The calculation of Ref. 19 yields the ionization potentials very well for Z=6-11, while for larger Z we can note a systematic lowering of the calculated values of Ref. 19 as compared with the data of Ref. 100, calculated data in Ref. 35 and all the more with the results of the calculations of Ref. 102. The calculated values of Ref. 103 for ions with Z=3-20 are close to the data of Ref. 19.

The results of the calculations allow one to detect evidently erroneous values of the ionization potentials of the

| Ζ | Experiment | Calculation | | | | | | |
|----|-------------------------------------|--|--------------------|--------|----------|--|--|--|
| | Experiment | [35] | [19, 14] | [106] | [102] | | | |
| | $1s^2 2p P_{3/2} - 1s^2 2p P_{1/2}$ | | | | | | | |
| 12 | 0,494 | 0,496 | 0,502 | 0,494 | _ | | | |
| 14 | 1,014 | 1,017 | 1,026 | 1,014 | _ | | | |
| 18 | 3,171 | 3,176 | 3,190 | 3,171 | _ | | | |
| 20 | 5,066 | 5,070 | 5,087 | 5,064 | 5,052 | | | |
| 26 | 15,962 | 15,970 | 15,997 | 15,965 | 15,930 | | | |
| 29 | 25,609 | 25,609 | 25,640 | 25,608 | — | | | |
| 32 | 39,142 | 39,131 | 39,164 | 39,140 | | | | |
| 36 | 64,932 | 64,899 | 64,929 | 64,932 | 64,798 | | | |
| 42 | 125,84 | 125,76 | 125,77 | 125,87 | - | | | |
| 54 | 372,38 | 371,78 | 371,61 | 372,36 | 371,72 | | | |
| 74 | - | 1498,1 | 1496,9 | 1502,6 | — | | | |
| 92 | | 4159,0 | 4155,7 | 4178,4 | 4176,3 | | | |
| | | 1s ² 2p ² P ₁ | $/2 - 1s^2 2s^2 5$ | 1/2 | | | | |
| 12 | 19,839 | 19,866 | 19,839 | 19,839 | _ | | | |
| 14 | 23,813 | 23,858 | 23,812 | 23,812 | _ | | | |
| 18 | 31,867 | 31,935 | 31,861 | 31,866 | | | | |
| 20 | 35,963 | 36,032 | 35,952 | 35,961 | 36,154 | | | |
| 26 | 48,604 | ³ 48,638 | 48,565 | 48,597 | 49,092 | | | |
| 29 | 55,155 | 55,157 | 55,099 | 55,155 | | | | |
| 32 | 61,901 | 61,847 | 61,811 | 61,902 | - | | | |
| 36 | 71,241 | 71,074 | 71,075 | 71,238 | 72,787 | | | |
| 42 | 86,102 | 85,680 | 85,747 | 86,102 | — | | | |
| 54 | 119,97 | 118,39 | 118,62 | 119,82 | 126,13 | | | |
| 74 | | 187,86 | 189,23 | 193,43 | 212,43 | | | |
| 92 | 280,72 | 275,26 | 285,35 | 280,68 | 323,15 - | | | |

TABLE III. Calculated and experimental values of the energy of lithium-like ions (in eV).

ions CuXXVII and ZnXXVIII given in the handbook, Ref. 105: 2560 and 2730 eV. The correct values are 2587.5 and 2782.6 eV, respectively, for Cu and Zn.

Table III compares the calculated values^{19,35,102,106} of the energy difference of the states $1s^22p\ ^2P_{3/2}-^2P_{1/2}$ and $1s^22p\ ^2P_{1/2}-1s^22s^2S_{1/2}$ with the experimental data.¹⁰⁷⁻¹¹⁰ The experimental data for large Z are limited.¹¹¹⁻¹¹⁵ As we see from the table, the calculated values³⁵ of the fine splitting of the energy of the 2p states coincide very closely with the experimental quantities. The difference from the recent measurements of this interval¹¹⁵ for ions with Z=26, 29, and 32 does not exceed 0.01 eV. For ions with Z=36, 42, and 54 the difference between the calculated values and the experimental data lies within the limits of experimental error. For Z=92 the difference between Ref. 35 and the calculated value¹⁰⁶ amounts to 0.4%.

The spacing $1s^2 2p {}^2P_{1/2} - 1s^2 2s {}^2S_{1/2}$ is given very accurately by the calculation of Ref. 106. The calculated values of Refs. 35 and 19 differ by several hundredths of an eV for Z < 32 and are lower for large Z than the data of Ref. 106. We note that the new calculated values¹⁰⁶ are substantially lower as compared with the old calculations¹⁸ by the same authors. The last column of Table III demonstrates how crudely the energy of the excited $1s^2 2p$ states is described by the calculation of Ref. 102 despite a rather good description of the energy of the ground state and the fine-splitting spacing. As was noted in Ref. 116 by the authors

| FABLE IV . | Comparison | of the | calculated | and | observed ^{117,118} | wave- |
|-------------------|---------------|--------|------------|------|-----------------------------|-------|
| lengths of lin | es (in nm) in | the sp | ectrum of | CIV. | | |

| Transition | λ_{obs} | $\lambda_{\rm calc}$ |
|------------|-----------------|----------------------|
| 4d6p | 165,44 | 165,47 |
| 4p6s | 165,39 | 165,46 |
| 4d6f | 163,77 | 163,80 |
| 4s—6p | 144,01 | 144,00 |
| 4f—7g | 135,30 | 135,30 |
| 4d—7f | 135,14 | 135,15 |
| 4p7d | 131,56 | 131,61 |
| 4d81 | 121,38 | 121,38 |
| 4s7p | 121,06 | 121,04 |
| 4p—8d | 118,44 | 118,50 |
| 3p4d | 110,8 | 110,88 |
| 3d4f | 116,9 | 116,88 |
| 4f—5g | 253,0 | 253,08 |

of Ref. 102, the correct values are obtained by calculating the screened Lamb shift. For the transitions 2s-3p, 2s-4p, 2p-3s, and 2p-4s, the calculated values obtained in Ref. 35 are close (within limits of 0.1 eV) to the experimental data of Edlen.²⁰

As an example of using the calculated values of the energy of the states of lithium-like ions, we compare in Table IV the wavelengths of the transitions in the spectrum of CIV with the experimental data of Refs. 117 and 118. The calculated values from Table IV describe the experimental values to a relative accuracy better than 5×10^{-4} .

Whenever one must calculate as accurately as possible a long chain (in n) of excited states for a given Z, one can do this by selecting the parameters A and B for the given nucleus, rather than from the condition of describing the entire set of Z values.

The analysis of the results of calculations shows that, when Z < 10, the relativistic effects are small, and the fundamental correction is that to the interaction energy of the electrons of different shells described by Eq. (22). Owing to this interaction the energy of the ground state of the lithium atom is increased by a factor of 1.6, while its dimension is decreased by the same factor. The magnitude of this correction for the $1s^22s$ state for Z=10 equals 21 eV, for Z=50 it amounts to 138 eV, and at large Z it depends linearly on Z. The decrease in the radius of the orbit of the outer electron owing to the interaction of (22) increases the splitting in the total angular momentum *j*. The interaction of (22) has an even greater effect on the multiplet shift of the 1s²2s level. For lithium the value of this shift exceeds fivefold the hydrogen-like value, while for Z=30the magnitude of the additional shift amounts to 3.5 eV. The magnitudes of the corrections are large; therefore the high accuracy of coincidence of the calculated data with the experimental results indicates that the interaction of the particles is fundamentally reflected correctly in the method being discussed. As compared with the semiempirical approach that employs the quantum defect,¹¹⁹ the method being discussed leaves undoubted the integervalued quantization of the angular momentum of the electrons, while transferring the difficulties into the region of describing the interaction of the particles.

| TABLE V. | Parameters | of the | 1snl states | of | helium-like | ions |
|----------|------------|--------|-------------|----|-------------|------|
|----------|------------|--------|-------------|----|-------------|------|

| State | A | В |
|---|---|--------------------------------------|
| $\frac{1 \text{ sns} ^{1} \text{S}_{0}}{1 \text{ snp} ^{1} \text{P}_{1}}$ $\frac{1 \text{ snp} ^{1} \text{D}_{2}}{1 \text{ sns} ^{3} \text{S}_{1}}$ $\frac{1 \text{ sns} ^{3} \text{P}}{1 \text{ snp} ^{3} \text{P}}$ | 0,306 - 0,143 0,0017 0,974 0,3775 | 0,140 0,05 0 0,104 -0,06 |
| lsnp ³ P Isnd ³ D | 0,3775 0,016 | - 0,06 0 |

The use of the Dirac function of (9) written not as a function of Z but of the radius of the orbit of the electron enables obtaining an accurate value of the fine-splitting interval without resorting to the screened charge of the nucleus, which is usually chosen empirically by using several constants.^{19,20}

1.4. 1sn/ states of helium-like ions

A helium-like ion in a 1snl state includes a hydrogenlike ion in the ground state to which an extra electron is combined having the angular momentum of motion $n\hbar$. The system of excited 1snl states of helium-like ions is more complex than the $1s^2nl$ states of lithium-like ions owing to the uncompensated spin moment of the 1s electron. Consequently helium-like ions are characterized by the presence of singlet and triplet terms. The energy of the 1snl states of helium-like ions equals

$$E(x,y) = \frac{2}{\alpha^2} \{ [1 + (\alpha^2/x^2)]^{1/2} - 1 \} - (Z/x) + \frac{1}{\alpha^2} \\ \times \{ [1 + (\alpha^2 n^2/y^2)]^{1/2} - 1 \} - [(Z-1)/y] \\ -AnF(x,y) - (Bx/ny),$$
(36)

where F(x,y) is the function of (22), and A and B are empirical parameters. The stationary states are determined by the condition of minimum energy

$$\partial E/\partial x = 0, \quad \partial E/\partial y = 0.$$
 (37)

One obtains from these conditions a system of equations analogous to (23) and (26), whose solution determines the radii of the stationary orbits x and y and the energy of the system in (36). The values of the parameters A and B for different states of helium-like ions are given in Table V.

The calculated energy differences of the states $1s^{2}S_{1/2} - 1snp^{3}P_{2}$ are compared with the experimental data^{107,109} in Table VI. Analogous results are obtained for other 1snl states. For small Z a high accuracy of description of experiment is obtained by using two empirical parameters. For large Z relativistic effects are essential. Equation (36) employs a relativistic expression for the kinetic energy. The main part of the multiplet shift of the energy levels can be described by using the correction of Eq. (9) D(y,n,j'), where y is the radius of the orbit of the outer electron, j' is the angular momentum of the outer electron (the sum of its orbital angular momentum and its intrinsic spin). For ${}^{3}P_{3/2}$ and ${}^{1}P_{1}$ states we have j'=3/2, and for ${}^{3}P_{0}$, ${}^{3}P_{1}$, ${}^{3}S_{1}$, and ${}^{1}S_{0}$ states j' = 1/2. These states differ from one another in the interaction with the inner electron. One must also take account of the spin-spin interaction and the spin-strange orbit interaction. We shall take account of these interactions empirically by selecting a dependence on the radius of the orbit of the outer electron y that describes the experimental data for ions having Z as large as possible. The chosen interpolative dependences for the multiplet shift of the energy of 1snl states of heliumlike ions are given in Table VII. For 1s2p ³P₂ states the correction terms from Table VII equal zero and the relativistic effects are completely determined by the relativistic dependence of the mass of the electron on its velocity. The energy difference of the ${}^{3}P_{2}$ and ${}^{3}P_{0}$ states equals

$$D(y,n,3/2) - D(y,n,1/2) - 0.66\alpha^2(n/y)^3$$
. (38)

| n | Nuclear charge Z | | | | | | |
|---|------------------|-------------|------------------|-------------|---------------|--------------|--|
| | 2 | 4 | 6 | 11 | 19 | 28 | |
| 2 | 3,6471 | 33,9953 | 87,6831 | 346,1276 | 1114,3160 | 2502,522 | |
| | 3,6239 | 33,9724 | 87,6714 | 346,1340 | 1114,3250 | 2502,521 | |
| 3 | 1,5811 | 14,0009 | 38,5536 | 152,9204 | 493,6567 | 1110,400 | |
| | 1,5810 | 14,0031 | 38,5566 | 152,9159 | 493,6590 | 1110,413 | |
| 4 | 0,8790 | 7,8178 | 21,5763 | 85,7708 | 277,1943 | 623,7641 | |
| | 0,8802 | 7,8194 | 21,5779 | 85,7671 | 277,1954 | 623,7705 | |
| 5 | 0,5587 | 4,9818 | 13,7674 | 54,7991 | 177,2066 | 398,8196 | |
| | 0,5599 | 4,9812 | 13,7702 | 54,7971 | 177,2086 | 398,8610 | |
| 6 | 0,3863 0,3876 | 3,4497 — | 9,5417 9,5419 | 38,0114 | 122,9654 — | 276,7576 | |
| 7 | 0,2829 0,2838 | 2,5293 | 7,0003 7,0005 | 27,9039 | 90,2910 — | 203,2198 | |

TABLE VI. Comparison of the calculated values³⁴ of the energy difference of the states $1s^{2}S_{1/2}$ and $1snp^{3}P_{2}$ (in eV) with the data of Refs. 107 and 109. Upper number—calculated value,³⁴ lower number—from Refs. 107 and 109.

TABLE VII. Multiplet shift of the energy of the 1snl states of helium-like ions.

| State | j' | Energy shift of the states |
|-----------------------------|-----|---|
| ³ P ₂ | 3/2 | $D(y, n, 3/2) + 0,001225[(n/2) - 1]/y^{2}$ |
| ³ P ₀ | 1/2 | $D(y, n, 1/2) + \{0,001225[(n/2) - 1]/y^{2}\} + 0,67 \alpha^{2}(n/y)^{3}$ |
| ³ P ₁ | 1/2 | $D(y, n, 1/2) + \{0,001225[(n/2) - 1]/y^{2}\} + 0,67 \alpha^{2}(n/y)^{3} + 0,67 \alpha^{2}[(n/y)^{3} - (11,6/y^{2})]$ |
| ³ S ₁ | 1/2 | $D(y, n, 1/2) + \{0,0025[(n/2) - 1]/y^{2}\} - 0,054 \alpha^{2}(n/y)^{3}$ |
| ¹ S ₀ | 1/2 | $D(y, n, 1/2) - \{0,0035[(n/2) - 1]/y^{2}\} + 0,67 \alpha^{2}(n/y)^{3}$ |
| ¹ P ₁ | 3/2 | $D(y, n, 3/2) - \{0,0016[(n/2) - 1]/y^{2}\} + 1,33\alpha^{2}[(n/y)^{3} - (11,6/y^{2})]$ |

The fundamental contribution for large Z comes from the splitting of the energy level of the outer electron that arises from the Dirac formula.

Using the calculated values of the energies of the 1snl states of the helium-like $ions^{34}$ and the energies of the helium-like ions in the ground state, ³⁶ we can calculate the energies and wavelengths of the transitions between any of the ${}^{1}P_{1}$, ${}^{1}S_{0}$, ${}^{3}P_{0,1,2}$, and ${}^{3}S_{1}$ states of the helium-like ions with Z=2-50, n=2-9. Table VIII compares the calculated values 19,34,125,127 of the wavelengths of the $1s2p-1s^2$ transitions with the precision measurements¹²⁰⁻¹²⁴ for the ions of argon, chromium, iron, and germanium. The calculated values³⁴ very exactly describe the experimental wavelengths. The results of the calculations of Ref. 19 are rather close to them. Apparently the appreciable difference from experiment of the results of the calculations of Ref. 125 involves an insufficiently correct calculation of the energy of the ground state of the helium-like ions. The calculated difference of the energies of the states $1s2p {}^{3}P_{2}-1s2s {}^{3}S_{1}$ is described by a calculation¹²⁶ by this same author with an accuracy of 0.01 eV, whereas the difference between the calculated value¹²⁵ and experiment for the transitions $1s2l-1s^2$ amounts to about 2-3 eV for Z=24-27. In Ref. 127 the correction of the results of the calculations of Ref. 19 also concerns the ground state of the helium-like ion (the energy for Ge is elevated by 0.98 eV).

Table IX shows our calculated wavelengths of the resonance transitions $1snp {}^{1}P_{1} - 1s^{2} {}^{1}S_{0}$ of the ion FeXXV (in Angström units) and the experimental data of Ref. 128. The experimental uncertainty of λ is estimated in Ref. 128 to be 0.0006 Å. As a rule, the difference between the calculated and experimental quantities does not lie outside the limits of experimental error.

Table X compares the experimental values of the wavelengths of the transitions $1s2p {}^{3}P_{2}-1s2s {}^{3}S_{1}$ of ions with $Z=10-36^{129-133}$ with the calculated data,³⁴ with the results of the calculations of Ref. 19, and with the calculations of Drake that were presented in Refs. 129–133. The relative accuracy of coincidence is 10^{-3} and better. This is a good accuracy if we take account of the fact that the transitions occur between states having the same values of *n*. Table X also compares the calculated value³⁴ with the calculated values of Refs. 134 and 14 for the ion U^{90+} . The $1s2p {}^{3}P_{2} - {}^{3}P_{0}$ spacing for U^{90+} coincides to high accuracy (10^{-4}) in the calculation of Ref. 34 (4256.55 eV) and in Ref. 134 (4256.05 eV).

1.5. States of beryllium-like and boron-like ions with equivalent electrons

Let us study the states $1s^22s^2$, $1s^22p^2$, and $1s^22p^3$. The presence in the second shell of equivalent electrons is common to these states. In the Bohr theory electrons are called equivalent (indistinguishable) that revolve about the nucleus in one circular orbit and are arranged at equal angular intervals, i.e., at the vertices of regular polygons. The

| Ion | Transition | λ_{exp} | | $\lambda_{	ext{theor}}$ | |
|---------|-------------------------------|----------------------|----------------------|-------------------------|----------------------|
| ArXVII | $1s2p {}^{1}P_{1} - 1s^{2}$ | 3.9491ª | 3.9486 ^e | 3.9492 ^f | 3.9490 ^a |
| | $1s2p^{3}P_{2} - 1s^{2}$ | 3.9657ª | 3.9656° | 3.9660 ^f | 3.9659ª |
| | $1s2p^{3}P_{1} - 1s^{2}$ | 3.9693ª | 3.9694° | 3.9695 ^r | 3.9693° |
| | $1s2p \ {}^{3}S_{1} - 1s^{2}$ | - | 3.9938° | 3.9943 ^r | |
| CrXXIII | $1s2p \ ^{1}P_{1} - 1s^{2}$ | 2.1818 ^b | 2.1817 ^f | 2.1821 ^f | 2.1826 ^g |
| | $1s2p {}^{3}P_{2} - 1s^{2}$ | 2.1886 ^b | 2.1884 ^e | 2.1886 ^f | 2.1895 ^g |
| | $1s2p {}^{3}P_{1} - 1s^{2}$ | 2.1927 ^b | 2.1925 ^e | 2.1926 ^r | 2.1934 ⁸ |
| | $1s2s {}^{3}P_{1} - 1s^{2}$ | 2.2035 ^b | 2.2032 ^e | 2.2035 ^r | 2.2044 ^g |
| FeXXV | $1s2p {}^{1}P_{1} - 1s^{2}$ | 1.8500 ^c | 1.8501° | 1.8504 ^f | 1.8508 ^g |
| | $1s2p {}^{3}P_{2} - 1s^{2}$ | 1.8552 ^c | 1.8552° | 1.8555 ^f | 1.8561 ^g |
| | $1s2p {}^{3}P_{1} - 1s^{2}$ | 1.8592 ^c | 1.8588 ^e | 1.8596 ^r | 1.8602 ^g |
| | $1s2s {}^{3}P_{1} - 1s^{2}$ | 1.8681 ^c | 1.8680 ^e | 1.8682 ^f | 1.8689 ^g |
| GeXXXI | $1s2p {}^{1}P_{1} - 1s^{2}$ | 1.20599 ^d | 1.20605 ^e | 1.20608 ^f | 1.20603 ^h |
| | $1s2p {}^{3}P_{2} - 1s^{2}$ | 1.20848 ^d | 1.20845 ^e | 1.20859 ^f | 1.20847 ^h |
| | $1s2p {}^{3}P_{1} - 1s^{2}$ | 1.21294 ^d | 1.21288 ^e | 1.21309 ^f | 1.21290 ^h |
| | $1s2s {}^{3}P_{1} - 1s^{2}$ | 1.21776 ^d | 1.21776 ^e | 1.21790 ^r | 1.21778 ^h |

TABLE VIII. Comparison of the calculated values of the wavelengths of the $1s2l-1s^2$ transitions (in Å) with the experimental data.

^e[120], ^b[121], ^c[123], ^d[124], ^e[34], ^f[19], ^g[125], ^b[127].

TABLE IX. Wavelengths of $1s_{\pi p} {}^{1}P_{1}-1s^{2} {}^{1}S_{0}$ transitions of the ion FeXXV.

| n | λ_{exp} | $\lambda_{\rm calc}$ | n | λ_{exp} | À calc |
|---|-----------------|----------------------|----|-----------------|--------|
| 2 | 1,8504 | 1,8501 | 7 | | 1,4325 |
| 3 | 1,5738 | 1,5730 | 8 | | 1,4258 |
| 4 | 1,4948 | 1,4945 | 9 | | 1,4212 |
| 5 | 1,4605 | 1,4607 | 10 | | 1,4180 |
| 6 | 1,4433 | 1,4430 | ∞ | | 1,4043 |

interaction of such electrons with one another decreases the binding energy of the electrons with the nucleus, which is equivalent to partial screening of the nuclear charge. The general formula for the screening coefficient σ in the electrostatic interaction of N equivalent electrons was derived by Bohr:¹

$$\sigma = \frac{1}{4} \sum_{s=1}^{N-1} \frac{1}{\sin(s\pi/N)}.$$
 (39)

Table XI gives some of the values of $\sigma(N)$ calculated by Bohr.

In calculating the energy of the $1s^2 2l^N$ states we shall start with the idea that the interaction of the 21 electrons with the nucleus and with the two inner 1s electrons is the same as in the $1s^22l$ states of the lithium-like ions. Moreover, we must take account of the energy of interaction of the 2l electrons with one another. Just as in the ground state of helium-like ions, this interaction is not restricted to the electrostatic interaction. Table XII presents the empirically obtained screening coefficients of the nuclear charge owing to the interaction with one another of the equivalent electrons in the $1s^2 2l^N$ configurations. These screening coefficients rather well reflect the general dependence on the number of electrons that is implied by the Bohr theory. At the same time there is an appreciable difference of the screening coefficients for a particular electronic configuration, depending on the type of term.

The multiplet shift of the energy states is substantial for large Z. The interpolated dependences for the multiplet shift of the energy of $1s^22l^N$ states are also given in Table XII.

The energy values of the states of beryllium-like and boron-like ions with Z=4-90 calculated in this way were obtained in Ref. 135. A comparison with the existing ex-

TABLE X. Comparison of the wavelengths (in Ångström units) of 1s2p ${}^{3}P_{2}$ -1s2s ${}^{3}S_{1}$ transitions.

| Z | Experiment | Calculation | | | |
|----------------------------------|--|---|---|---|--|
| | | Ref. 34 | Refs 19, 14 | Drake | |
| 10 20 22 29 36 92 | $1248,11 \pm 0,03 [129]466,8 \pm 0,1 [130]389,49 \pm 0,07 [131]206,65 \pm 0,08 [132]111,15 \pm 0,08 [133]$ | 1247,71 466,64 389,47 206,85 111,20 2,7434 | 1247,72 466,82 389,55 206,83 111,22 2.7435 | 1248,09 466,90 389,57 206,75 2,7463 | |

TABLE XI. Screening coefficients according to Bohr¹.

| N | 2 | 3 | 4 | 5 | 6 |
|------|------|-------|-------|-------|-------|
| σ(N) | 0,25 | 0,577 | 0,957 | 1,376 | 1,827 |

perimental data^{100,110} and the calculated results¹³⁶ is given in the same place. We note the rather high accuracy of the description in Ref. 135 of the energy of the 1s²2s² ¹S₀ and 1s²2p² ³P_{0,2} states of beryllium-like ions (as a rule the deviation does not exceed hundredths of an electron volt). The difference of the energies of the states 1s²2p² ³P₂-³P₀ (the extremes in the multiplet) is described by the function D(y,2,1/2) to an accuracy of 1% (see Table XIII below). For the states 1s²2p² ¹D₂, ¹S₀ one obtains not very exact results for ions with small Z=4-9. The values of the energies of the 1s²2p³ states are described by the calculation of Ref. 135, mainly to an accuracy of 0.1 eV.

States with equivalent electrons are also found in the ions of the sequence of helium and lithium, in which simultaneously two electrons occur in the excited state. These ions are observed in a plasma of multiply charged ions via lines that are satellites to the resonance lines of hydrogen-like and helium-like ions, respectively.

The energy of the $2p^2$ states of helium-like ions can be represented in analytic form, analogously to the energy of the ground state of helium-like ions¹³

$$E(Z) = \frac{2}{\alpha^2} \left[\left\{ 1 - \left[\alpha^2 (Z - \sigma)^2 / 4 \right] \right\}^{1/2} - 1 \right] - K.$$
 (40)

The radius of the orbit along which the electrons move equals

$$x = \frac{4\{1 - [\alpha^2 (Z - \sigma)^2 / 4]\}^{1/2}}{Z - \sigma}.$$
 (41)

The screening coefficient σ and the parameter K are selected on the basis of the experimental data. The best agreement for $2p^2$ ³P, ¹D states is obtained for values of σ that coincide with the mutual screening coefficients of $2p^2$ electrons in the $1s^22p^2$ ³P, ¹D states of beryllium-like ions (see Table X). This means that the presence of the 1s electrons does not affect the law of interaction of the $2p^2$ electrons with one another. The parameter K for $2p^2$ ³P

TABLE XII. Screening coefficients σ owing to interaction of the electrons in $1s^22l^N$ configurations and the multiplet shift of energy levels.

| State | σ | σ_{B} | Energy shift |
|--|---|---|---|
| $1s^{2}2s^{2} {}^{1}S_{0}$ $1s^{2}2p^{2} {}^{3}P_{2}$ $1s^{2}2p^{2} {}^{3}P_{1,0}$ $1s^{2}2p^{2} {}^{1}D_{2}$ $1s^{2}2p^{3} {}^{4}S_{3/2}$ $1s^{2}2p^{3} {}^{2}D_{5/2}$ $1s^{2}2p^{3} {}^{2}P_{3/2}$ | 0,2757 0,329 0,329 0,3637 0,447 0,66 0,702 0,743 | 0,25 0,25 0,25 0,25 0,25 0,577 0,577 0,577 | 1,75D(y, 2, 1/2) 0,25D(y, 2, 1/2) 1,25D(y, 2, 1/2) D(y, 2, 1/2) D(|

TABLE XIII. Comparison with the experimental data of Ref. 110 of the calculated values of Refs. 135 and 136 of the spacings $1s^22p^2 {}^{3}P_2 {}^{-3}P_0$ of beryllium-like ions and the calculated values of Refs. 19 and 137 of the spacings $2p^2 {}^{3}P_2 {}^{-3}P_0$ of helium-like ions (in cm⁻¹).

| Z | $1s^2 2p^2 {}^3P_2 - {}^3P_0$ | | | 2p ^{2 3} P | $_{2} - {}^{3}P_{0}$ |
|--------|-------------------------------|--------|-------|---------------------|----------------------|
| | [135] | [136] | [110] | [137] | [19] |
| 4 | 3,63 | _ | 3,43 | 66,4 | |
| 5 | 22,7 | | 22,4 | 174 | |
| 6 | 78,5 | 83 | 76,5 | 378 | 410 |
| 7 | 201,2 | 209 | 198 | 724 | 621 |
| 8 | 429,5 | 441 | 424,5 | 1267 | 1336 |
| 9 | 811 | 828 | 804 | 2070 | 2119 |
| 10 | 1403 | 1426 | 1394 | 3205 | 3245 |
| [11] | 2271 | 2300 | 2248 | 4754 | 4772 |
| 12 | 3489 | 3527 | 3467 | 6807 | 6511 |
| 13 | 5141 | 5189 | 5113 | 9466 | 9000 |
| 14 | 7321 | 7377 | 7306 | 12837 | 12140 |
| 15 | 10130 | 10192 | 10091 | 17042 | 16044 |
| 16 | 13680 | 13739 | 13631 | 22208 | 20823 |
| 17 | 18093 | 18131 | 18060 | 28474 | 26050 |
| 20 | 37863 | 37523 | - | 55399 | 48551 |
| 22 | 58016 | 56834 | — | 81833 | 71362 |
| 25 | 102228 | 98108 | — | 138105 | 113322 |
| 28 | 168146 | 158655 | _ | 219732 | 176836 |

states equals 0.38 eV, and for 2p² ¹D states 0.76 eV. For large Z the same dependences for the multiplet shifts are adopted in the calculations as for the corresponding states of the beryllium-like ions from Table X. The calculated energy values of the doubly excited states of helium-like ions were obtained in this way in Ref. 137. For Z=6-12the data of Refs. 137 and 19 agree to an accuracy of 0.1 eV. For large Z calculation¹⁹ yields a somewhat larger value of the energy; for Z=26 the difference amounts to 5 eV (relative difference 10^{-3}). The values of the wavelengths of the transitions $2p^2 {}^{3}P_0$ -1s2p ${}^{1}P_1$ and $2p^2 {}^{1}D_2$ -1s2p ${}^{1}P_1$ calculated by using the energies of the $2p^2$ states from Ref. 137 and the energies of the $1s2p P_1$ states from Ref. 34 are smaller than those from the calculation of Ref. 19 by approximately one milli-Angström unit. Table XIII compares the calculated values for the spacings $1s^22p^2 {}^{3}P_2 - {}^{3}P_0$ (Ref. 135) and $2p^2 {}^{3}P_2 - {}^{3}P_0$ (Ref. 137) with the results of the calculations of Refs. 19 and 136 and with the experimental data given in Ref. 110. For Z < 17 the results of the calculations of Ref. 135 for the interval $1s^22p^2 {}^{3}P_2 - {}^{3}P_0$ differ from the data of Ref. 110 by 0.2-2%. The difference of the results of the calculations of Ref. 136 from the data of Ref. 110 is from two to three times larger. For Z=26the value¹³⁵ of the spacing $1s^22p^2 {}^3P_2 - {}^3P_0$ is 0.70 eV larger than in Ref. 136. For large Z the difference increases and reaches 6.88 eV for Z=45. The calculated data for $1s^{2}2p^{2} {}^{3}P_{2} - {}^{3}P_{0}$ (Ref. 135) and $2p^{2} {}^{3}P_{2} - {}^{3}P_{0}$ (Ref. 137) follow the rule: the spacing $2p^2 {}^{3}P_2 - {}^{3}P_0$ for a helium-like ion with a given Z is somewhat smaller than the spacing $1s^22p^2 {}^{3}P_2 - {}^{3}P_0$ for the beryllium-like ions with a nuclear charge larger by two units.

The fine splitting of the states $2p^2 {}^{3}P_2 - {}^{3}P_0$ calculated in this way for Z < 13 agrees well with the results of the calculations of Ref. 19. For large Z the data of Ref. 19 for the fine splitting of the $2p^{2}$ ³P states are lower than the calculated values of Ref. 137, being lower by a factor of 1.24 for Z=28. In the comparison of the calculated values^{34-36,135} obtained in the same way as in Ref. 137 with the experimental results for other states of multielectron ions, the difference in the fine splitting is usually less than 1%, while for ions with Z > 20 it is less than 0.1%. To the same degree of accuracy also the calculated values in Ref. 19 for the intervals $1s^{2}2p^{2}P_{3/2}-{}^{2}P_{1/2}$ of lithium-like ions coincide with the results of Ref. 35. Such a large difference of the values 137 of the intervals $2p^{2} {}^{3}P_{2}-{}^{3}P_{0}$ from the calculated values of Ref. 19 can involve the cruder description of the energy of doubly excited states in Ref. 19 as compared, e.g., with the states of lithium-like ions.

The values of the energy of doubly excited states $1s2p^2 {}^4P$ of the lithium-like ions were determined by starting with the idea that the law of interaction of the 2p electrons with the 1s electron is the same as for the states $1s2p {}^3P$ of the helium-like ions (with the same parameters). The interaction of the 2p electrons with one another is described by using the same parameters (screening coefficient σ) as for the $2p^2 {}^3P$ states of the helium-like ions and $1s^22p^2 {}^3P$ of the beryllium-like ions.

The values of the energy difference of the states $1s {}^{2}S_{1/2} - 1s2p^{2} {}^{4}P_{5/2}$ were obtained for ions with Z=2-100 by this type of calculations in Ref. 137. Comparison of these data with the results of calculation of Ref. 19 showed that very good agreement of the results of the calculations¹³⁷ and the data of Ref. 19 exists for Z < 12, while for larger Z the energy values¹³⁷ are somewhat smaller. The difference for Z=26 amounts to 5 eV. The fine splitting of the states $1s2p^{2} {}^{4}P_{5/2}$, ${}^{4}P_{1/2}$ was calculated in the same way as the fine splitting of the states $1s2p^{3}P_{2} - {}^{3}P_{0}$ of the helium-like ions.

1.6. The energy of Rydberg states of ions

States of complex ions with a high excitation value n are called Rydberg states. For large n the energy of transition between states of different n approaches the energy in the hydrogen-like ions. Transitions between states having the same values of n cannot be described by the hydrogen-like approximation, and even for very large n the states of the ions maintain their individuality.

In line with the expansion in (30) we have

$$\frac{1}{2\pi} \int_0^{2\pi} \frac{\cos \varphi d\varphi}{(x^2 + y^2 - 2xy \cos \varphi)^{1/2}} = \frac{x}{2y^2} + \frac{3x^3}{16y^4} + \dots$$
(42)

When $x/y \leq 1$, we may keep only the first term in Eq. (42). Then in the nonrelativistic approximation the energy of the states $1s^C nl$ (where C is the number of electrons in the 1s state) equals

$$E(x,y) = C\left(\frac{1}{2x^2} - \frac{Z - \sigma}{x}\right) + \frac{n^2}{2y^2} - \frac{Z - C}{y}$$
$$-\frac{CAnx}{2y^2} - \frac{CBx}{ny}.$$
 (43)

This expression describes the energy of the highly excited states of helium-like (C=1, $\sigma=0$) and lithium-like (C=2, $\sigma=0.3125$) ions.

The conditions of minimum energy yield:

$$-\frac{1}{x^3} + \frac{Z - \sigma}{x^2} - \frac{An}{2y^2} - \frac{B}{ny} = 0,$$
 (44)

$$-\frac{n^2}{y^3} + \frac{Z - C}{y^2} + \frac{CAnx}{y^3} + \frac{CBx}{ny^2} = 0.$$
 (45)

Neglecting the influences of the outer electron on the radius of the inner orbit $(x=1/(Z-\sigma))$, we obtain from Eq. (45)

$$y = \frac{n^2 - [CAn/(Z-\sigma)]}{Z - C + [CB/n(Z-\sigma)]}.$$
 (46)

The energy difference of the states $1s^{C}$ and $1s^{C}nl$ equals

$$E = -\frac{\{Z - C + [CB/n(Z - \sigma)]\}^2}{2\{n^2 - [CAn/(Z - \sigma)]\}}.$$
(47)

It makes no sense to solve Eqs. (44) and (45) more exactly and use a larger number of terms in the expansion (42) in obtaining an approximate solution, since one can easily obtain an exact numerical solution (as is done). The value of Eqs. (46) and (47) lies in their graphic quality, while the region of applicability is determined by comparison with the exact solution.

The high accuracy of description by Eq. (47) of the energy of highly excited states of helium-like ions has been shown in Ref. 34.

Comparison with the numerical solution indicates that Eq. (47) is a good approximation also for small n in the case in which relativistic effects are inessential.

In describing the energy of excited states one often employs the concept of the quantum defect. The energy of the excited states is represented in the form:

$$E_n = -\frac{(Z-C)^2}{2(n-\delta(Z))^2}.$$
 (48)

Equation (47) allows one to obtain an analytic dependence of the quantum defect on Z:

$$\delta(Z) = \frac{CA}{2(Z-\sigma)} + \frac{CB}{(Z-\sigma)(Z-C)}.$$
(49)

Another form of representation of the energy of complex ions is the use of the screening coefficients σ :

$$E_n = -\frac{(Z - \Sigma)^2}{2n^2}.$$
 (50)

We can obtain from Eq. (47) the dependence of the screening coefficient σ on the nuclear charge Z and the principal quantum number *n* for each type of states of helium-like and lithium-like ions:

$$\Sigma(Z,n) = C - \frac{CA(Z-C)}{2n(Z-\sigma)} - \frac{CB}{n(Z-\sigma)}.$$
 (51)

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Here the function F(x,y) is determined by Eq. (23). The stationary states are found from the condition of minimum energy

$$\partial E/\partial x = 0, \quad \partial E/\partial y = 0, \quad \partial E/\partial u = 0.$$
 (53)

One obtains from these conditions a system of three equations whose solution determines x, y, and u, and then the energy of the state

$$E(x,y,u) = \frac{C_1}{\alpha^2} \left[\left(1 + \frac{\alpha^2}{x^2} \right)^{-1/2} - 1 \right] + \frac{C_2}{\alpha^2} \left[\left(1 + \frac{4\alpha^2}{y^2} \right)^{-1/2} - 1 \right] + \frac{C_3}{\alpha^2} \left[\left(1 + \frac{\alpha^2 n^2}{u^2} \right)^{-1/2} - 1 \right] - \frac{C_1 C_2 B_{12} x}{2y} - \frac{C_1 C_3 B_{13} x}{nu} - \frac{C_2 C_3 B_{23} y}{nu}.$$
 (54)

Equation (52) is written with account taken of the quantization of the angular momentum of the electrons in each orbit, while it also takes account of the relativistic

1.7. General expression for the energy of ions having three electron shells

Ions with three electron shells form a large class of states of the type $1s^2mlnl'$, $1s^22l^2nl'$, $1s^22lnl'^2$, etc., as well as analogous states for ions with one electron in the 1s state. In calculating the energy of such systems, we shall start with the idea that the interaction law of the electrons in any two electron shells does not depend on the presence or number of electrons in the third shell. This hypothesis is analogous to the principle of linearity (or superposition) in electrical and wave phenomena.

Let x, y, and u be the radii (in units of a_0) of the first, second, and third electron shells, C_1 , C_2 , and C_3 the number of electrons in these shells, and σ_1 , σ_2 , and σ_3 the screening coefficients arising from interaction of the equivalent electrons in a given shell, while A_{ik} and B_{ik} are the interaction constants in Eqs. (22) and (24) of the electrons of different shells (with numbers *i* and *k*).

The energy of the system with three electron shells equals

$$E(x,y,u) = \frac{C_1}{\alpha^2} \left[\left(1 + \frac{\alpha^2}{x^2} \right)^{1/2} - 1 \right] - \frac{C_1(Z - \sigma_1)}{x} + \frac{C_2}{\alpha^2} \left[\left(1 + \frac{4\alpha^2}{y^2} \right)^{1/2} - 1 \right] - \frac{C_2(Z - C_1 - \sigma_2)}{y} - 2A_{12}C_1C_2F(x,y) - \frac{C_1C_2B_{12}x}{2y} + \frac{C_3}{\alpha^2} \left[\left(1 + \frac{\alpha^2n^2}{u^2} \right)^{1/2} - 1 \right] - \frac{C_3(Z - C_1 - C_2 - \sigma_3)}{u} - A_{13}C_1C_3nF(x,u) - A_{23}C_2C_3nF(y,u) - \frac{C_1C_3B_{13}x}{nu} - \frac{C_2C_3B_{23}y}{nu}.$$
 (52)

TABLE XIV. Parameters A_{23} and B_{23} of the states of beryllium-like ions.

| State | A ₂₃ | B ₂₃ |
|--|-----------------|-----------------|
| $1s^2 2sns^3 S_1$ | 0,460 | 0,085 |
| $1s^2 2sns S_0$ | 0,310 | 0,095 |
| $1s^{2}2snp^{3}P_{0,1,2}$ | 0,321 | 0,070 |
| $1s^2 2pns^3 P_{0,1,2}$ | 0,346 | 0,039 |
| $1s^{2}2pnp^{3}P_{0+2}$ | 0,190 | 0,039 |
| 1s ² 2p <i>n</i> p ¹ P | 0,376 | 0,040 |
| 1s ² 2pnp ³ D _{1,2,3} | 0,326 | 0,040 |
| $1s^2 2p_{II}p^3 S_1$ | 0,223 | 0,066 |
| $1s^2 2pnd D_2$ | 0,043 | 0,136 |
| 1s ² 2snd ³ D _{1,2,3} | 0,190 | 0 |

dependence of the mass of an electron on its velocity. Moreover, one must take account of the multiplet shift of the energy and radiation effects.

1.8. 1s²2/n/' states of berylium-like ions

The $1s^2 2lnl'$ states of beryllium-like ions can be of the type 1s²2snl' with excitation of one outer electron, or of the type $1s^2 2pnl'$, when both outer electrons are excited. The interaction of the electrons of the core $(1s^22s \text{ or } 1s^22p)$ is the same as in the corresponding states of the lithium-like ions. The energy of interaction of the outer electron with the inner 1s electrons is written in the same way (and with the same constants) as in the lithium-like ions. One selects the interaction constants of the outer electron with the electrons of the second shell by comparison with the experimental data. The parameters A_{23} and B_{23} of a number of such states of beryllium-like ions are given in Table XIV. The values of the energy difference of the states $1s^22l$ and $1s^2 2lnl'$ of ions with Z=4-50, n=3-6 calculated in this way are given in Ref. 138. Experimental data for the energy of excited states of beryllium-like ions exist for ions of relatively small Z. Table XV compares the energy differences of the states $1s^2 2l$ and $1s^2 2l3l'$ (Ref. 138) calculated with the parameters from Table XIV with the data of Refs. 107 and 109. In most cases the coincidence is better than 0.1 eV.

The energy of excited states with large values of n is known for a series of beryllium-like ions of nitrogen.¹⁰⁸ Comparison of these data with the values calculated by the method presented above shows that the calculation¹³⁸ rather well matches the values of Ref. 108.

The multiplet energy shift is mainly determined by the function D(u,n,j') [see Eq. (9)], where j' is the sum of

TABLE XV. Comparison of the calculated values of the energy (in eV) of the $1s^22/nl'$ states¹³⁸ of beryllium-like ions with the data of Refs. 107 and 109.

| | · | | | | |
|----|--|--|--|-----------------|--|
| z | E[138] | E[107, 109] | E[138] | E[107, 109] | |
| | $1s^{2}2s^{2}S_{1/2}$ | - 1s ² 2s3s ³ S ₁ | $1s^{2}2s^{2}S_{1/2} - 1s^{2}2s^{3}p^{3}P_{2}$ | | |
| 4 | 2.8630 | 2.8653 | 1.9965 | 2.0191 | |
| 5 | 9,0260 | 9.0661 | 7.2627 | 7.3025 | |
| 6 | 18,2979 | 18.3497 | 15.6411 | 15.6885 | |
| 7 | 30,6337 | 30,6964 | 27,0866 | 27,1397 | |
| 8 | 46,0184 | 46,0670 | 41,5810 | 41,6101 | |
| 9 | 64,4463 | -`64,5075 | 59,1156 | 59,1593 | |
| 10 | 85,9159 | | 79,6863 | 79,7271 | |
| 11 | 110,4280 | 110,4566 | 103,2907 | 103,2969 | |
| 12 | 137,9849 | 137,9579 | 129,9280 | 129,7877 | |
| | 1s ² 2p3s ³ P ₂ | $-1s^{2}2s^{2}s_{0}$ | $1s^2 2s^2 S_{1/2} -$ | $1s^22s3d^3D_3$ | |
| 4 | 10,6828 | | 1,6812 | 1,6290 | |
| 5 | 22,5293 | 22,5253 | 6,5243 | 6,4767 | |
| 6 | 38,2055 | 38,2143 | 14,4399 | 14,4103 | |
| 7 | 57,6934 | 57,7196 | 25,4034 | 25,3932 | |
| 8 | 80,9935 | 81,0144 | 39,4046 | 39,4126 | |
| 9 | 108,1137 | 108,1248 | 56,4383 | 56,4646 | |
| 10 | 139,0658 | 139,0841 | 76,5020 | 76,5462 | |
| 11 | 174,0552 | 173,8566 | 99,5941 | 99,6496 | |
| 12 | 212,5277 | 212,4917 | 125,7139 | 125,6969 | |
| | 1 | 1 | I | 1 | |

the orbital angular momentum and the spin of the outer electron, and u is the radius of the orbit of the outer electron. The fine splitting of the states $1s^22snp {}^{3}P_2$, ${}^{3}P_0$ is described analogously to the splitting of the states $1snp {}^{3}P_2$, ${}^{3}P_0$ of the helium-like ions:

$$\Delta E({}^{3}\mathrm{P}_{2}-{}^{3}\mathrm{P}_{0}) = D(u,n,3/2) - D(u,n,1/2) + 0.185\alpha^{2}(n/u)^{3}.$$

The energy difference between the extreme components of the fine structure of the states $1s^22snd {}^3D_3$, 3D_1 equals

$$\Delta E({}^{3}\mathrm{D}_{2} - {}^{3}\mathrm{D}_{0}) = D(u, n, 5/2) - D(u, n, 3/2) + 0.033\alpha^{2}(n/u)^{3}.$$

Table XVI compares the calculated values of the fine splitting of the states $1s^22s^3p \, {}^3P_2 - {}^3P_0$ and $1s^22s^3d \, {}^3D_3 - {}^3D_1$ of beryllium-like ions with the data of Refs. 107 and 109. The agreement is good, while at large Z one can note a certain nonmonotonicity of the experimental values.

The spacing between the extreme components of the triplet of the state $1s^22pns \ ^3P_2 - \ ^3P_0$ is very close to the splitting of the states $1s^22p \ ^2P_{3/2}, \ ^2P_{1/2}$ of the lithium-like

TABLE XVI. Comparison of the calculated values¹³⁸ with the data^{107,109} for the fine splitting of the energy of the states $1s^22s3p {}^{3}P_2, {}^{3}P_0$ and $1s^22s3d {}^{3}D_3, {}^{3}D_1$ of beryllium-like ions (in cm⁻¹). The upper number is from Ref. 138, and the lower from Refs. 107 and 109.

| | 5 | 6 | 7 | 8 | 10 | 11 | 12 | 13 |
|---|--------------|----------------|----------------|----------------|----------------|------------|-------------|--------------|
| $\overline{{}^{3}D_{3}-{}^{3}D_{1}}$ | 4.72 4.74 | 18.79 18.75 | 51.54 51.20 | 114.2 113.6 | 387.8 388.2 | 635 600 | 983 1000 | 1453 1400 |
| ³ D ₃ - ³ D ₁ | 0.93 | 4.22 3.91 | 12.4 12.2 | 29.0 30.3 | 104.8 | 175 158 | 276 265 | 416 424 |

TABLE XVII. Experimental¹⁰⁷ and calculated¹³⁸ values of the spacings $1s^22p^{3s} {}^{3}P_2 - {}^{3}P_0$ and $1s^22p {}^{2}P_{3/2} - {}^{2}P_{1/2}$ (in cm⁻¹).

| Interval | Atomic number Z | | | | | |
|---|-----------------|------|-------|-------|-------|-----|
| | 4 | 5 | 6 | 7 | 8 | 9 |
| Experiment: ${}^{3}P_{2} - {}^{3}P_{0}$ | 5,97 | 30,7 | 101,9 | 244,8 | 505,3 | 918 |
| ${}^{2}P_{3/2} - {}^{2}P_{1/2}$ | 6,6 | 34,1 | 107,1 | 258,7 | 532,5 | 977 |
| Calculation ${}^{3}P_{2} - {}^{3}P_{0}$ | 5,98 | 30,1 | 97,2 | 237,8 | 493,0 | 912 |
| ${}^{2}P_{3/2} - {}^{2}P_{1/2}$ | 7,5 | 36,0 | 110,6 | 263,8 | 537,2 | 982 |

ions. Table XVII compares the values of these spacings for 3s states on the basis of the experimental data presented in Ref. 107. Apparently this splitting is mainly due to the interaction of the 2p electron, i.e., this is the difference in energy of the states $1s^22p(^2P_{1/2})$ 3s and $1s^22p(^2P_{1/2})$ 3s:

$$\Delta E({}^{3}\mathrm{P}_{2} - {}^{3}\mathrm{P}_{0}) = D(y, 2, 3/2) - D(y, 2, 1/2),$$

where y is the radius of the orbit of the 2p electron. The values of the spacing ${}^{3}P_{2} - {}^{3}P_{0}$ calculated in this way are also given in Table XVII.

The $1s^22pns$ ${}^{3}P_2 - {}^{3}P_0$ splitting depends in an unusual way on the quantum number n of the outer electron; it is another evidence of the influence on the fine splitting of the interaction of (22). In the case of $1s^2np$ states the attraction by the inner shell decreases the radius of the orbit of the 2p electron and increases the fine splitting ${}^{2}P_{3/2} - {}^{2}P_{1/2}$. In the state $1s^2 2pns$ the attraction by the outer ns shell increases the radius of the orbit of the 2p electron as compared with 1s²2p states. In agreement with Eq. (9), this decreases its fine splitting. The influence of the outer nselectron declines with increasing n. Therefore with increasing *n* the fine splitting of the states $1s^22pns^3P_2$, 3P_0 increases, approaching the value for the 1s²2p states. We can see this behavior of the fine splitting from Table XVIII, which presents the experimental results for nitrogen¹⁰⁸ and the calculated values.¹³⁸

There is a large class of excited states with this type of behavior of the fine splitting. The spacing between the extreme components of the multiplet of the $1s^22p^2({}^{3}P)ns {}^{4}P$ states is close to the energy difference of the states $1s^22p^2 {}^{3}P_2$, ${}^{3}P_0$, and of the states $1s^22s2p({}^{3}P)ns {}^{4}P^0$ to $1s^22s2p {}^{3}P_2 - {}^{3}P_0$. The situation is analogous for the states $1s^22s^22pns {}^{3}P$, $1s^22s^22p^2ns {}^{4}P$, and $1s^22s2p^2({}^{4}P)ns {}^{5}P$, and a number of states of magnesium-like, aluminum-like, and other ions. The unusual behavior of the fine splitting with varying *n* can serve as a good distinctive indicator of such

TABLE XVIII. Spacings $1s^22pns$ ${}^{3}P_{2}-{}^{3}P_{0}$ of the beryllium-like ion of nitrogen (cm⁻¹).

| n | E_{exp} (Ref. 107) | E _{calc} (Ref. 138) |
|---|----------------------|-------------------------------|
| 3 | 244,8 | 237,8 |
| 4 | 252,8 | 256,1 |
| 5 | 256,9 | 260,4 |
| 6 | 269,8 | 262,1 |

states, and the calculated quantities that are obtained are useful in deciphering experimental spectra, especially of ions with large Z.

1.9. The 1s²2f²nl' states of boron-like ions

The experimental data on the energy levels of boronlike ions are highly limited, both in multiplicity of ionization and in degree of excitation. For the excited states $1s^2 2l^2 nl'$ in Refs. 107 and 109 data exist for the ions with Z < 10-15 for n=3, while for large n results exist only for ions with Z=6, 7. To a considerable extent this is explained by the lack of reliable values that would make it possible to identify the corresponding lines in the measured spectra. The method of calculation given above [Eqs. (52)-(54)] allows one to obtain calculated values of the energy of the $1s^2 2l^2 nl'$ states of boron-like ions. The interaction of the electrons of the $1s^22s^2$ or $1s^22p^2$ core is the same as for the corresponding states of the beryllium-like ions. The energy of interaction of the outer electron with the inner 1s electrons is written in the same way (and with the same constants) as in the lithium-like ions. One selects the interaction constants of the outer electron with the electrons of the second shell by comparison with the experimental data. The parameters A_{23} and B_{23} for such states of boron-like ions are given in Table XIX.

The multiplet shift of the energy levels of the $1s^22s^2nl$ states with a given value of the total angular momentum *j* is described by the function D(u,n,j) [see Eq. (9)]. The fine splitting of the energy of the states $1s^22s^2np\ ^2P_{3/2},\ ^2P_{1/2}$ equals

$$\Delta E({}^{2}\mathrm{P}_{3/2} - {}^{2}\mathrm{P}_{1/2}) = D(u, n, 3/2) - D(u, n, 1/2).$$

For $1s^22s^2nd$ states we have

TABLE XIX. Parameters A_{23} and B_{23} of $1s^22l^2nl'$ states of boron-like ions.

| State | A ₂₃ | B ₂₃ |
|--|-----------------|-----------------|
| 1 s ² 2s ² ns ² S | 0,405 | 0,10 |
| 1s ² 2s ² ns ² P | 0,317 | 0,06 |
| 1s ² 2s ² np ² D | 0,148 | -0,8 |
| $1s^{2}2p^{2}(^{3}P)ns^{4}P$ | 0,363 | 0 |
| $1s^22p^2(^3P)np^4P$ | 0,254 | 0,076 |
| $1s^{2}2p^{2}(^{3}P)np^{4}D$ | 0,282 | 0,081 |
| $1s^{2}2p^{2}(^{3}P)np^{4}S$ | 0,1855 | 0,059 |
| 1s ² 2p ² (³ P)nd ⁴ P | 0,05 | 0,024 |

| · Z | $1s^{2}2s^{2}S_{0} - 1s^{2}2s^{2}3s^{2}S_{1/2}$ | | $1s^{2}2s^{2}S_{0} - 1s^{2}2s^{2}3p^{2}P_{3/2}$ | | $1s^{2}2s^{2}S_{0}^{2} - 1s^{2}2s^{2}3d^{2}D_{5/2}$ | |
|-----|---|--------------|---|--------------|---|--------------|
| | E [139] | E [107, 109] | E [139] | E [107, 109] | E [139] | E [107, 109] |
| 5 | 3,3346 | 3,3340 | 2,2875 | 2,2707 | (.5053 | 1.5077 |
| 6 | 10,1238 | 9,9338 | 8,0349 | 8.0509 | 6.3410 | 6.3373 |
| 7 | 20,0818 | 20,0017 | 16,9712 | 16,9810 | 14.3312 | 14.3056 |
| 8 | 33,1300 | 33,0770 | 29,0136 | 29.0417 | 25,4133 | 25.3963 |
| 9 | 49,2415 | 49,1949 | 44,1275 | 44,1491 | 39.5596 | 39.5406 |
| 10 | 68,4056 | 68,3643 | 62,2959 | 62,2707 | 56.7559 | 56.7102 |
| 11 | 90,6180 | 90,5505 | 83,5097 | 83,4745 | 76,9941 | 76,9923 |
| 12 | 115,878 | 115,925 | 107,764 | | 100,269 | 100,263 |
| 13 | 144,187 | 144,111 | 135,056 | 134,945 | 126,578 | 126,591 |
| 14 | 175,547 | 175,538 | 165,383 | - | 155,919 | 155,982 |
| 15 | 209,962 | 210,036 | 198,747 | | 188.291 | 188,454 |

TABLE XX. Comparison of the calculated values¹³⁹ of the energy (in eV) of 1s²2s²3l states of boron-like ions with Refs. 107 and 109.

$$\Delta E(^{2}\mathrm{D}_{5/2}-^{2}\mathrm{D}_{3/2})=D(u,n,5/2)-D(u,n,3/2).$$

The energy values of a number of $1s^22s^2nl$ states calculated in this way for boron-like ions with Z=5-50, n=3-6 are given in Ref. 139. Table XX compares the calculated values of the energy difference of the states $1s^22s^2$ and $1s^22s^23l$ that have been obtained with the data of Refs. 107 and 109. The difference of the calculated from the experimental values lies within the limits of hundredths of an electron volt.

The spacings between the extreme components of the multiplets of the states $1s^22p^2({}^{3}P)ns {}^{4}P_{5/2}$, ${}^{4}P_{1/2}$ and $1s^22p^2({}^{3}P)np {}^{4}D_{7/2}$, ${}^{4}D_{1/2}$ were calculated starting with the idea that this is the spacing $1s^22p^2 {}^{3}P_2 - {}^{3}P_0$ distorted by the influence of the outer *ns* or *np* electron, i.e.,

$$\Delta E = D(y,2,3/2) - D(y,2,1/2).$$

The influence of the outer *ns* (or *np*) electron enters via the value of the radius *y* of the orbit of the 2p electrons, which decreases somewhat with increasing degree of excitation of the outer electron *n*, approaching the value of the radius for the beryllium-like ion $1s^22p^2$ ³P. The calculated value for the spacing $1s^22p^2({}^{3}P)3s$ ${}^{4}P_{5/2} - {}^{4}P_{1/2}$ for nitrogen is 182 cm⁻¹, which is close to the value 166 cm⁻¹ given in Ref. 109. For the spacings $1s^22p^2({}^{3}P)3p$ ${}^{4}D_{7/2} - {}^{4}D_{1/2}$ and $1s^22p^2({}^{3}P)4p$ ${}^{4}D_{7/2} - {}^{4}D_{1/2}$ calculated values of 189.6 and 197.5 cm⁻¹ were obtained in place of 171.4 and 192.7 cm⁻¹ from Ref. 109. We see that the calculation qualitatively correctly reflects the influence of the outer electron. For the stronger binding in the case of a 3s electron the magnitude of the spacing is somewhat smaller than in the case of a 3p electron: with increasing *n* the binding of the outer electron declines, while the splitting increases.

Apparently the $1s^22p^2({}^{3}P)ns {}^{4}P_{3/2} - {}^{4}P_{1/2}$ spacing, just like the $1s^22pns {}^{3}P_1 - {}^{3}P_0$ spacing, involves the interaction of the outer electron. That is, its value is

$$\Delta E = D(u, n, 3/2) - D(u, n, 1/2).$$

Here *u* is the radius of the orbit of the outer electron, and *n* is its principal quantum number. Table XXI compares the values of the spacings $1s^22p^2({}^{3}P)3s {}^{4}P_{3/2} - {}^{4}P_{1/2}$ and $1s^22p3s {}^{3}P_1 - {}^{3}P_0$ calculated in this way with the data of Refs. 107 and 109. While the values of the spacings

 ${}^{4}P_{5/2} - {}^{4}P_{1/2}$ and ${}^{3}P_2 - {}^{3}P_0$ increase weakly with increasing *n*, the spacings ${}^{4}P_{3/2} - {}^{4}P_{1/2}$ and ${}^{3}P_1 - {}^{3}P_0$ decline with increasing *n* (for large *n* as $1/n^3$). Therefore, for large *n*, with a practically invariant spacing between the extreme components of the multiplet, the spacings ${}^{4}P_{3/2} - {}^{4}P_{1/2}$ and ${}^{3}P_1 - {}^{3}P_0$ approach zero.

1.10. Quartet $1s2s(^{3}S)n$ - and $1s2p(^{3}P)n$ states of lithium-like lons

Lithium-like ions having a vacancy in the K shell have been insufficiently studied, both experimentally and theoretically, especially in the case of high excitations (n > 3). More complete data exist for the light ions: lithium,¹⁴⁰ beryllium,¹⁴¹ boron,¹⁴² and carbon.¹⁴³ Apparently the quartet states of the ion CIV have been studied in greatest detail.¹⁴³ For Z > 6 experimental data exist only for individual ions of the isoelectronic sequence, e.g., for the ion TiXX in Ref. 144. Calculated values for the energies of the transitions $1s2/3l' - 1s^22l$ and $1s2/3l' - 1s^23l'$ for ions with Z=6-33 were obtained in Ref. 145. We note also the calculated data of Ref. 146 for the ion ArXVI with n=2-4.

The lithium-like ions with the electronic configuration 1s2lnl' (n>3), together with the excited states of beryllium-like and boron-like ions, are ions with three electron shells. It is assumed in the calculations that the inter-

TABLE XXI. Comparison of the calculated values (in cm⁻¹) of the spacings $1s^22p^3s \ ^3P_1-^3P_0$ and $1s^22p^23s \ ^4P_{3/2}-^4P_{1/2}$ with the data of Refs. 107 and 109.

| Ζ | $1s^2 2p 3s^3 P_1 - {}^3 P_0$ | | 1s ² 2p ² 3s ⁴ | $P_{3/2} - {}^{4}P_{1/2}$ |
|----|-------------------------------|--------------|---|---------------------------|
| | Ecalc | E [107, 109] | $E_{\rm calc}$ | E [107, 109] |
| 4 | 1,67 | 2,0 | | |
| 5 | 10,2 | 9,8 | 2,5 | - |
| 6 | 32,8 | 33,3 | 17,3 | _ |
| 7 | 79,5 | 79,2 | 54,9 | 66,7 |
| 8 | 163,1 | 162,1 | 129,5 | 144 |
| 9 | 298,4 | 281 | 259,1 | 261 |
| 10 | 504,2 | 495 | 465,3 | |
| 11 | 800,3 | 805 | 772,9 | - |
| 12 | 1210,2 | 1094 | 1210,7 | 1228 |

TABLE XXII. Parameters A_{23} and B_{23} of states of beryllium-like and lithium-like ions.

| State | Parameter | | |
|--|--|---|---|
| Beryllium-like ion | Lithium-like ion | A ₂₃ | B ₂₃ |
| 1 s ² 2sns ³ S 1 s ² 2snp ³ P 1 s ² 2pnp ³ S 1 s ² 2pnp ³ P 1 s ² 2pnp ³ D 1 s ² 2pns ³ P 1 s ² 2snd ³ D | 1 s2s(³ S) <i>n</i> s ⁴ S 1 s2s(³ S) <i>n</i> p ⁴ P 1 s2p(³ P) <i>n</i> p ⁴ S 1 s2p(³ P) <i>n</i> p ⁴ P 1 s2p(³ P) <i>n</i> s ⁴ P 1 s2p(³ P) <i>n</i> s ⁴ P 1 s2p(³ P) <i>n</i> d ⁴ D | 0,460 0,321 0,223 0,190 0,326 0,346 0,190 | 0,085 0,070 0,066 0,039 0,040 0,039 0 |

action of the core electrons (1s2s or 1s2p) is the same as in the corresponding states of the helium-like ions. The energy of interaction of the outer electron with the inner 1s electron is written in the same way (and with the same constants) as in the helium-like ions. The interaction constants of the electrons of the second and third shells were chosen in the calculations of the energy of the 1s²2*lnl*' states of the beryllium-like ions. Thus, in calculating the energy of the quartet 1s2*lnl*' states of the lithium-like ions, none of the constants employed in the calculations was chosen from experimental data on these ions. The parameters A_{23} and B_{23} of the $1s^2 2lnl'$ states of the beryllium-like ions and the 1s2lnl' quartet states of the lithium-like ions corresponding to them are given in Table XXII. The energy difference between the extreme components of the fine structure of the states $1s2snp {}^{4}P_{5/2}$, ${}^{4}P_{1/2}$ and $1s2snd {}^{4}D_{7/2}$, ${}^{4}D_{1/2}$ is described in the same way as for the analogous states of the beryllium-like ions.

Values of the energy difference of the states 1s2l-1s2lnl' with Z=3-50, n=3-6 were obtained in Ref. 147. Table XXIII compares the calculated values of the

TABLE XXIII. Comparison of the calculated values of the energy (in eV) of quartet states of lithium and the lithium-like ion of carbon¹⁴⁷ with the data of Refs. 140 and 143.

| Transition | Z = 3 | | Z = 6 | |
|--|---------|---------|---------|---------|
| | E [147] | E [140] | E [147] | E [143] |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})3s^{4}S$ | 2,738 | 2,776 | 29,769 | 30,006 |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})4s^{4}S$ | 1,277 | | 15,741 | 15,758 |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})3p^{4}P$ | 2,077 | 2,083 | 27,200 | 27,319 |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})4p^{4}P$ | 1,068 | 1,061 | 14,796 | |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})5p^{4}P$ | 0,651 | 0,646 | 9,302 | |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})3p^{4}P$ | 1,876 | 1,880 | 26,194 | 26,187 |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})4p^{4}P$ | 0,994 | 0,990 | 14,410 | 14,458 |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})5p^{4}P$ | 0,616 | 0,612 | 9,112 | 9,162 |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})3p^{4}S$ | ì,993 | _ | 26,545 | 26,513 |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})3p^{4}D$ | 2,109 | | 27,322 | 27,256 |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})4p^{4}D$ | 1,075 | _ | 14,832 | 14,864 |
| $1s2p^{3}P_{2} - 1s2p(^{3}P_{2})3s^{4}P$ | 2,462 | 2,498 | 27,737 | 27,834 |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})3d^{4}D$ | 1,695 | 1,696 | 25,450 | 25,722 |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})4d^{4}D$ | 0,924 | 0,923 | 14,113 | 14,181 |
| $1s2s^{3}S_{1} - 1s2s(^{3}S_{1})5d^{4}D$ | 0,581 | 0,584 | 8,963 | 8,988 |

of carbon with the data of Refs. 140 and 143. In most cases the difference does not exceed hundredths of an electron volt. Reference 147 also studied the influence of the outer electron on the fine splitting of the 1s2p states. The good accuracy of the calculated description of the energy of the quartet states of the lithium-like ions indicates the great predictive potential of the method of calculation being used.

1.11. Calculation of the energy of the excited states of the hydrogen molecule

energy of the quartet states of lithium and lithium-like ions

The spectra of emission and absorption of electromagnetic waves by molecules are a rich source of information on the properties of complex substances. Molecular spectra differ from atomic spectra in the far greater number of lines. This involves the fact that, in addition to the transitions between different electronic states (analogous to transitions in atoms), molecules can absorb and emit energy in connection with the vibrations of the nuclei with respect to the equilibrium position (vibrational energy levels) and in connection with the rotation of the molecule as a whole (rotational energy levels).

Some very simple molecular systems are the molecular ion H_2^+ and the molecule H_2 of hydrogen. They have been widely studied, both experimentally and theoretically. One can find the quantum-mechanical methods of calculating their ground state in many monographs (see, e.g., Ref. 148). The parameters of the energy characteristics of the molecules (energies of the electronic states, vibrational and rotational constants) are collected in Ref. 149. The excited electronic states of molecules have been considerably less studied, especially by calculation and theory.

A very simple and pictorial model of the electronic configurations of the hydrogen molecule H_2 was proposed by N. Bohr.^{1,2} In this model the hydrogen molecule in the ground state amounts to a system of two hydrogen nuclei, at an equal distance from which two electrons revolve in a single circular orbit in a plane perpendicular to the line joining the nuclei. The angular momentum of each electron is $mvr = \hbar$. The electronic configuration is the same as in the helium atom in the ground state. The model of the ground state of the ion of H_2^+ is analogous, but with only one electron in the orbit.

A calculation of the energy of the excited electronic states based on the Bohr method is given in Ref. 40. In the Bohr model one can represent the hydrogen molecule in excited electronic states as a system consisting of an inner H_2^+ ion in the ground state and an outer electron in various excited states revolving in a circular orbit in the same plane as the inner electron. From the standpoint of the interaction of the electron excited states. The orbital angular momentum of the outer electron takes on the quantized values $n\hbar$ (n=2, 3,...). In the absence of rotation of the electron (which coincides with the projection on the axis of the molecule) is conserved.

Let us present the calculation of the energy of the ground state of the H_2^+ ion. Let x be the radius of the electron ring, and r the distance between the nuclei (in units of a_0). Then, under the condition that the orbital angular momentum of the electron is quantized, the energy of the system equals (in atomic units):

$$E(x,r) = -2/[x^2 + (r^2/4)]^{1/2} + (1/r) + (1/2x^2).$$
(55)

The conditions of minimum energy $\partial E/\partial x=0$, $\partial E/\partial r=0$ yield a system of equations for finding x and r:

$$\frac{2x}{(x^2+r^2)^{3/2}} - \frac{1}{x^3} = 0,$$
$$\frac{2r}{(x^2+r^2)^{3/2}} - \frac{1}{2r^2} = 0.$$

The solution of this system yields:

$$x/r=2(4^{2/3}-1)^{1/2},$$

 $x=2/(4^{2/3}-1)^{2/3}, r=4/(4^{2/3}-1)^{2}.$

The value that is obtained of the energy of the ground state of the H_2^+ ion equals E = -0.43884 atomic units in place of the experimental value $E_{exp} = -0.59739$ atomic units.¹⁵¹ Evidently in the calculation of the energy of the H_2^+ ion by the Bohr method there is not the degree of coincidence with experiment as in the case of the hydrogen atom. Nevertheless we shall hesitate to discard it. The Bohr method in its initial form is inapplicable to ions with a number of electrons greater than unity. However, as is shown above, on its basis it has been possible to construct a graphic semiempirical model that enables one to describe to high accuracy the energy of multielectron ions.

Let us introduce into the expression for the energy of the system (55) an additional term—D/r, with the same empirical constant D, so as to obtain the experimental value of the energy of the ground state of the ion H_2^+ . In this case we have

$$E(x,r) = -\frac{2}{\left[x^2 + \left(r^2/4\right)\right]^{1/2}} + \frac{1-D}{r} + \frac{1}{2x^2}.$$
 (56)

The experimental value of the energy is obtained for D=0.2364. Here we have x=0.91487. Close-lying values of x are obtained for the same energy of the state also in the case in which the plane of the orbit of the electron lies at an arbitrary distance from the nuclei. The correction introduced in this way corresponds as though to a decrease in the interaction of the nuclei in a narrow region in the direction of the axis joining them, while leaving unchanged the Coulomb interaction of the nuclei with the electron (i.e., in the remaining region of solid angle). We note that models with an effective charge of the nuclei are used in the theory of molecular spectra.¹⁵⁰

We can write the energy of the excited states of the H_2 molecule in the same form as for the helium atom:

$$E(x,y,r) = -\frac{2}{[x^2 + (r^2/4)]^{1/2}} + \frac{1-D}{r} + \frac{1}{2x^2}$$

$$-\frac{2}{[y^{2}+(r^{2}/4)]^{1/2}}+\frac{1}{y}+\frac{n^{2}}{2y^{2}}$$
$$-\frac{An}{2\pi}\int_{0}^{2\pi}\frac{\cos\varphi d\varphi}{(x^{2}+y^{2}-2xy\cos\varphi)^{1/2}}$$
$$-\frac{Bx}{ny}.$$
 (57)

Here x and y are the radii of the orbits of the inner and outer electrons, r is the internuclear distance (in units of a_0), and A and B are empirical constants. For one-electron excited states of the hydrogen molecule we shall use the same numerical values of A and B as for the analogous states of helium-like ions.³⁴ These parameters depend on L and S and do not depend on n and j. That is, they describe the entire series of excited states having different n values.

The stationary states are determined from the condition of minimum energy

$$\partial E/\partial x = 0, \quad \partial E/\partial y = 0, \quad \partial E/\partial r = 0.$$
 (58)

The solution of the system of equations (58) yields values of x, y, and r at the point of minimum energy for a given value of n. For a fixed internuclear distance r the conditions $\partial E/\partial x=0$ and $\partial E/\partial y=0$ determine the curve of the dependence on r of the energy of the system $E_n(r)$.

For large *n* the values of x and r approach the values for the free ion H_2^+ . In this case we have x/y < 1 (r/y < 1), and we can expand the integrand in Eq. (3) in a series. As a result the expression for the energy of the outer electron E(y) acquires the form

$$E(y) = -\frac{2}{[y^2 + (r^2/4)]^{1/2}} + \frac{1}{y} + \frac{n^2}{2y^2} - \frac{Anx}{2y^2} - \frac{Bx}{ny}.$$
 (59)

The equation for finding y is obtained from the condition $\partial E/\partial y=0$. When r/y < 1, we can derive an analytic expression for y. However, since the numerical solution of system (58) causes no difficulties, we present below the results of the numerical calculations.

The calculated energy of the outer electron equals the sum of its kinetic energy and the energy of interaction with the nuclei and the inner electron. Here the energy of a bound state is negative, while a zero energy corresponds to an outer electron and an ion separated to infinity. In spectroscopy one usually takes the energy of the ground state to be zero. The energy of an electron-ion system separated to infinity equals the ionization potential of the ground state. The energy of the excited states introduced in Ref. 151 amounts to the energy of excitation of a given state from the ground state, where the values of T_e pertain to the energy minimum. One takes as the ionization potential in Ref. 149 the energy difference between the lowest vibrational state of the ground electronic state of the ion and the lowest vibrational state of the ground electronic state of the molecule. Therefore the energy corresponding to calculation obtained on the basis on Ref. 149 of the state of the outer electron equals the energy difference T_e of the excited state and the ionization potential of the ground state of the molecule (with account taken of the correction to the energy of the lowest vibrational states). This quantity with sign reversed amounts to the ionization potential of the excited state.

A comparison of the experimental values of the ionization potentials of the one-electron excited states of the He atom¹⁰⁷ and the excited states of the H₂ molecule corresponding to them,¹⁴⁹ as well as the calculated values of the ionization potentials of the excited states of the H₂ molecule obtained from the same classification of states as in the helium atom shows that one can establish a correspondence of the energy levels in the molecular classification and the energy levels of the one-electron excited states of the hydrogen molecule in the classification of the analogous states of the helium atom. It turns out that the molecular states $np\sigma^{-1}\Sigma_{u}^{+}$ rather closely coincide with the states 1sns $1S_0$ of this same molecule calculated in the helium-like approximation. Analogously one can establish the correspondence of the states $np\pi$ ${}^{1}\Pi_{u}$ and 1snp ${}^{1}P_{1}$, $np\sigma {}^{3}\Sigma_{u}^{+}$ and $1sns {}^{3}S_{1}$, $np\pi {}^{3}\Pi_{u}$ and $1snp {}^{3}P$, and $nd\sigma {}^{3}\Sigma_{g}^{+}$ and $1snd {}^{3}D$. For most states the binding energy of the outer electron calculated in the helium-like approximation agrees with the experimental data¹⁴⁹ within limits of 0.05 eV. We note that the calculated energies of the excited states of the H₂ molecule obtained by other methods differ from experiment appreciably more (0.15-0.25 eV).¹⁵¹ We see from Ref. 40 the closeness of the energy of the excited states of the hydrogen molecule and the helium atom. The calculated difference in energy of the states of H₂ and He is manifested in the fact that the correction to the energy of the hydrogen atom expressed by the two last terms in Eq. (5) is proportional to the radius of the orbit of the inner electron x. While for the He^+ ion this radius equals 0.5, for the molecular ion H_2^+ it amounts to 0.915. In agreement with the increase in the ratio of these radii, the correction to the energy of the excited states for H_2 is increased as compared with He.

Without presenting the results of the calculations, we note also the closeness (to an accuracy of 0.1 eV) of the energies of the excited states of the beryllium atom and the He₂ molecule isoelectronic with it: $ns\sigma {}^{3}\Sigma_{u}^{+}$ of the He₂ molecule and $1s^{2}2snp {}^{3}P$ of the Be atom; $np\sigma {}^{3}\Sigma_{g}^{+}$ and $1s^{2}2sns {}^{3}S$; and $np\pi {}^{3}\Pi_{g}$ and $1s^{2}2snd {}^{3}D$. We emphasize again that the ionization potentials of excited states are being compared. The excitation energies of these states differ considerably owing to the energy difference of the ground state of the isoelectronic atom and molecule.

2. STATES OF ATOMS FOR A FIXED ATOMIC VOLUME. SEMIEMPIRICAL EQUATION OF STATE OF SOLIDS

2.1. Energy of atomic states at fixed atomic volume

The states of free multielectron, multiply charged ions were studied above by the Bohr method. This same method allows one to study the states of atoms with restricted volume.³⁸ The energy values of the states of free atoms (occupying an unbounded volume in space) are the result of the interaction of the electrons with the nucleus and with one another for quantized (integer-valued in units of \hbar) values of the angular momentum of each electron.

These states are realized in a rarefied gas, in which one can neglect the interaction of the atoms. The presence of neighboring atoms substantially alters the character of the interaction of the particles in an atom. In a solid each atom is surrounded by a large number of neighbors, and each atom possesses a bounded volume of space. For a free atom a transition to an excited state or ionization can occur, whereby the electron lies at a great distance from the nucleus or is completely removed to infinity (in ionization). In a solid an atom can undergo transition to an excited state within one electroneutral cell or can undergo transition to a state of a positive ion in a given cell and a negative ion in any adjacent cell. In any case the electron lies here at a distance from the nucleus that does not exceed the radius of the elementary atomic cell of the solid.

Let us study some features of the excitation of atoms and ions involving a bounded volume per atom. First we turn to the very simple case of atomic hydrogen. The values of the energy of states of the hydrogen atom allowed by the conditions of quantization of the angular momentum $mvr = n\hbar$ are determined by the expression

$$E_n = \frac{n^2}{2x^2} - \frac{1}{x},$$
 (60)

where $x = r/a_0$, a_0 is the Bohr radius, and E_n is in atomic units.

For the free hydrogen atom we have $r_n = n^2 a_0$, $E_n = -1/2n^2$, and $E_{kin} = 1/2n^2$. For fixed volume (x constant), E_n is determined by Eq. (60), while $E_{kin} = n^2/2x^2$ increases with increasing *n*. This is the reason for the sharp variation of the positions of the energy levels as compared with the free atom.

The positions of the energy levels of atomic hydrogen for different values of the volume of the atom (different x) are shown in Fig. 1. If the dimension of the excited atom $x_n < x$, then in rarefied atomic hydrogen the energy levels of the free atom are excited, while for large *n* the energy levels at fixed atomic volume become excited. The expression for the energy of the transitions $\Delta E_{mn} = (m^2 - n^2)/2x^2$ is analogous to the quantum-mechanical solution of the problem of a particle in a rectangular potential well.

The quantum-mechanical methods of calculation⁴² yield a qualitatively similar pattern (the calculation pertains to the ground state of the hydrogen atom): with decreasing dimension of the spherical cavity within which the atom lies, the energy value increases. The difference consists in the fact that this increase begins at values of the radius of the cavity considerably exceeding the mean radius of the electron distribution. Figure 2 shows the dependence on the radius of the atom of the energy of the ground state of the hydrogen atom obtained in the model of the Bohr atom³⁸ and by the quantum Monte Carlo method in Ref. 42. The Bohr model as applied to atoms contained in a solid yields closer values of the pressure upon compression of the atom (see below) than, e.g., upon using the Hartree–Fock method.⁴³



FIG. 1. Energy levels of atomic hydrogen for different values of the radius x of the atomic cell.

2.2. Energy of an atom in a solid. Metallic lithium^{37,38}

We shall assume that atoms in a solid (including metals) retain their individuality. We shall first take up the case in which interaction with the adjacent atoms is absent, and study the effects involving the boundedness of the volume per atom. Using the model of the atom presented above, we shall study metallic lithium as a set of elementary atomic cells containing a lithium atom in the ground state.

The energy of a free lithium atom in a state with principal quantum number n of the outer electron is determined by the expression

$$E(x,y) = (2/\alpha^{2}) \{ [1 + (\alpha^{2}/x^{2})]^{1/2} - 1 \} - (5.375/x) + (1/\alpha^{2}) \{ [1 + (\alpha^{2}n^{2}/y^{2})]^{1/2} - 1 \} - 1/y - \frac{An}{\pi} \int_{0}^{2\pi} \frac{\cos\varphi \,d\varphi}{(x^{2} + y^{2} - 2xy\cos\varphi)^{1/2}} - \frac{2Bx}{ny}$$
(61)

under the condition $\partial E/\partial x=0$, $\partial E/\partial y=0$. In the case in which the volume of the atom is bounded (i.e., a concrete value of the radius of the outer electron y is fixed), the energy value is calculated from Eq. (61) with the fulfillment of only one condition $\partial E/\partial x=0$.

The pressure upon compressing the elementary atomic cell equals

$$P = -\frac{\partial E}{\partial V} = -\frac{\partial E}{\partial y} \frac{\partial y}{\partial V}.$$

The volume of the elementary cell is $V=4\pi ky^3a_0^3/3$, where k is the packing coefficient. Let the equilibrium value of the radius of the atom contained in the atomic cell of the solid be y_0 . Then we have

$$P = -\frac{1}{4\pi k y^2 a_0^3} \frac{\partial E}{\partial y} = -\frac{y_0^3}{3V_0 y^2} \frac{\partial E}{\partial y} = -\frac{\rho_0 N_A}{3A} \frac{y_0^3}{y^2} \frac{\partial E}{\partial y}.$$
(62)

Here $V_0 = 4\pi k y_0^3 a_0^3/3 = A/\rho_0 N_A$, A is the atomic mass, ρ_0 is the density of the substance under equilibrium conditions, and N_A is Avogadro's number. We shall assume that the compression of the electron ring occurs similarly to the compression of a solid, i.e., $y_0/y = \sigma^{1/3}$, where $\sigma = V_0/V$. In this case we have

$$P = \frac{\rho_0 N_{\rm A}}{A} \sigma^2 \frac{\partial E}{\partial \sigma}.$$
 (63)

We obtain from Eq. (61)

$$\frac{\partial E}{\partial y} = -\frac{n^2}{y^3 [1 + (\alpha^2 n^2 / y^2)]^{1/2}} + \frac{1}{y^2} + \frac{2Bx}{ny^2} + \frac{An}{\pi} \int_0^{2\pi} \frac{(y - x\cos\varphi)\cos\varphi \,d\varphi}{(x^2 + y^2 - 2xy\cos\varphi)^{3/2}}.$$
 (64)

The numerical solution reduces for a given y to finding the value of x from the equation $\partial E(x,y)/\partial x=0$, and then proceeding to determine the energy and pressure from Eqs. (61) and (62) for the found value of x.

We can obtain an approximate solution by using the expansion of (42) in a series in Legendre polynomials of the integrand that enters into the expression (61) for the energy. In this case in the nonrelativistic approximation the energy of the free lithium atom is expressed as follows:

$$E(x,y) = \frac{1}{x^2} - \frac{5.375}{x} + \frac{n^2}{2y^2} - \frac{1}{y} - \frac{Anx}{y^2} - \frac{2Bx}{ny}$$



FIG. 2. Dependence on the radius of the atomic cell of the energy of the ground state of the hydrogen atom. *I*—calculation based on the model of the Bohr atom, ³⁸ 2—calculation by the quantum Monte Carlo method.⁴²

The energy of the outer electron including its kinetic energy and the energy of interaction with the atomic core containing the nucleus and the two electrons in the K shell equals

$$E(y) = [(n^2 - 2Anx)/2y^2] - \{[1 + (2Bx/n)]/y\}.$$
(65)

The results of the numerical calculations imply that, for not too great compressions, the interaction with the outer electron has little influence on the radius of the orbit of the inner electrons and their energy. Therefore we shall assume in an approximate solution that the radius of the orbit of the inner electrons equals the radius of the orbit of these electrons in the helium-like ion of lithium x=1/2.6875=0.3721. In this case the radius of the orbit of the free lithium atom (under the condition $\partial E/\partial y=0$) equals

$$y_n = (n^2 - 2Anx) / [1 + (2Bx/n)].$$
 (66)

We can rewrite the expression for the energy (65) in the form

$$E = \left(1 + \frac{2Bx}{n}\right) \left(\frac{y_n}{2y^2} - \frac{1}{y}\right) = 2E_n \left(\frac{\sigma^{2/3}}{2} - \sigma^{1/3}\right).$$
(67)

Here y_n is the equilibrium radius of the free atom in (66), $E_n = (1 + 2Bx/n)/2y_n$ is the binding energy of the outer electron in the free atom, and $\sigma = (y_n/y)^3$.

The value of the energy per unit mass of substance differs from (67) in the factor N_A/A :

$$E = \frac{2E_n N_A}{A} \left(\frac{\sigma^{2/3}}{2} - \sigma^{1/3} \right).$$
 (68)

Substituting the expression (67) for $E(\sigma)$ into Eq. (63), we obtain the value of the pressure

$$P(\sigma) = \frac{2E_n N_A \rho_n}{3A} (\sigma^{5/3} - \sigma^{4/3}).$$
 (69)

Comparison of the values of the energy and the pressure calculated by the approximate formulas (68) and (69) and those obtained by numerical solution from Eqs. (61) and (62) shows that, when $\sigma < 2$, the difference is less than 1%, for $\sigma < 3$ less than 2%, and for $\sigma < 10$ less than 7%. This implies the possibility of using a simple form of the equation of state (68) and (69) in practical calculations over a broad range of compressions. A natural limitation involves electronic phase transitions in which the parameters E_n , y_n , and ρ_0 vary.

A calculation using the energy of the free lithium atom in the ground state yields a value of the pressure for the same degree of compression σ smaller by a factor of 1.42 than the experimental value for metallic lithium. The constancy of this ratio as a function of σ enables one to use the magnitude of the energy of the state of the atom in the solid as an empirical parameter. We can assume that the new energy value effectively takes account of the interaction with the neighboring atoms.

We have studied the case in which the system is displaced from a situation of equilibrium by compression of the orbit of the outer electron with conservation of the given quantum state. The excitation of states of electrons

TABLE XXIV. Values of the pressures (in GPa) in the cell of metallic lithium at normal density upon excitation of $1s^2nl$ states.

| n | 2 | 3 | 4 | 5 |
|--------------------|----|----|-----|-----|
| 1s ² ns | 0 | 46 | 112 | 198 |
| 1s ² np | 11 | 61 | 130 | 220 |

with other values of n and l in the atoms of a solid at fixed volume per atom implies the creation of states far from a position of equilibrium. If excited states are created in a substance at normal density, then this excited cell can be treated as an excited cell of the free atom compressed by the external pressure to a dimension smaller than the equilibrium value for the given excitation.

The pressure values (in gigapascals) that arise in the cell of metallic lithium at normal density in the excitation of 1s²nl states are given in Table XXIV (without taking account of the influence of the neighbors).

2.3. Semiempirical equation of state

The expression for the internal energy (68) and for the pressure (69) on the zero isotherm can be used for solids as a semiempirical equation of state with the parameters E_n and ρ_n , which are determined by comparison with experiment.

We obtain the following expression for the square of the velocity of sound:

$$c^{2} = \frac{\mathrm{d}P}{\mathrm{d}\rho} = \frac{1}{\rho_{n}} \frac{\mathrm{d}P}{\mathrm{d}\sigma} = c_{0}^{2} (5\sigma^{2/3} - 4\sigma^{1/3}),$$

where

$$c_0^2 = \frac{2E_n N_A}{9A}$$

is the square of the velocity of sound for $\sigma = 1$.

The bulk elastic modulus is determined by the expression

$$B = -V \frac{dP}{dV} = \sigma \frac{dP}{d\sigma} = \rho c^2 = B_0 (5\sigma^{5/3} - 4\sigma^{4/3}).$$
(70)

Here $B_0 = \rho_n c_0^2$ is the value of the elastic modulus for $\sigma = 1$.

Taking as the reference origin for the energy its value for $\sigma = 1$, we can rewrite the expression for the pressure (69) and the energy (68) in the form

. ...

$$P(\sigma) = 3B_0(\sigma^{5/3} - \sigma^{4/3}),$$

$$E(\sigma) = \frac{9B_0}{2\rho_0}(\sigma^{1/3} - 1)^2.$$
(71)

We obtain the following expression for the derivative of the bulk modulus B with respect to the pressure:

$$B' = \frac{\mathrm{d}B}{\mathrm{d}P} = \frac{25\sigma^{1/3} - 16}{3(5\sigma^{1/3} - 4)}.$$

When $\sigma = 1$ the value of B' is 3, when $\sigma > 1$ B' decreases ($\sigma=2.0, B'=2.25$), and when $\sigma < 1$ it increases ($\sigma=0.9$,

B'=3.27). In contrast to the equation of state of Murnahan and Birch⁶⁶ in this case B' is not a parameter of the equation of state.

Different regions of the $P(\rho)$ curve obtained experimentally can correspond to different phases of the substance. One can determine the parameters of each phase from two experimental points $P_1(\rho_1)$ and $P_2(\rho_2)$ on the corresponding region

$$\rho_n^{1/3} = \frac{P_2 \rho_1^{5/3} - P_1 \rho_2^{5/3}}{P_2 \rho_1^{4/3} - P_1 \rho_2^{4/3}},$$

$$3B_0 = \frac{P_2}{(\rho_2 / \rho_n)^{5/3} - (\rho_2 / \rho_n)^{4/3}}.$$
(72)

In the Mie–Grüneisen form the thermal component of the pressure is $P_t = \Gamma \rho E_t$. The Grüneisen coefficient Γ is determined by calculation on the basis of the dependence (71). In the Dugdale–Macdonald approximation⁶⁶ we have

$$\Gamma = \frac{2\sigma^{1/3} - 1}{3\sigma^{1/3} - 2}.$$
(73)

The parameters $\rho_{0 \text{ K}} = \rho_n$ and B_0 for a number of substances are given in Refs. 37-39. Here $\rho_{0 \text{ K}}$ is the density of the compact substance at zero temperature. For substances for which these parameters do not vary in the process of compression one can use the handbook values (e.g., Ref. 152). Usually the equilibrium density of the substance at zero temperature is considered to be known and is not included among the empirical parameters of the equation of state. However, as will be shown below, for many substances in compression a change of phase state (or electronic structure) occurs in which the parameters of the equation of state are changed. Therefore it seems justified to consider the density ρ_n and the bulk modulus B_0 to be empirical parameters of the equation of state (71).

Let us compare the obtained calculated values of the pressure on the normal isotherms of a number of substances with the data of Ref. 153. In this comparison it is essential to take account of the difference of the density under normal conditions (T = 300 K) from the density at T = 0 K and the existence here of a thermal component of the pressure. To a very large degree this pertains to small degrees of compression.

For metallic lithium in the pressure range 1-50 GPa the difference is 1%. For sodium up to $\sigma = 1.5$ the difference is 2%, while at large σ our calculated values are lower than in Ref. 153 (by 20% at P=50 GPa). Here they coincide rather closely with the data for static compression.¹⁵⁴ For beryllium the difference is 1.5% for P=1-50 GPa. For vanadium, niobium, molybdenum, and tungsten up to a pressure of 100 GPa, the difference is several percent, and 20% at p=400 GPa. In Ref. 155 pressures were calculated in lithium at a temperature T=0 K up to a compression $\sigma=100$. When P < 50 GPa they exceed the values of Ref. 153 and ours^{37,38} by a factor of 1.1-1.25, and when $\sigma=10$ they exceed our values 1.1-fold, and 1.5-fold at $\sigma=100$. Up to a density of lithium of 10^4 g/cm³ calculated values exist¹⁵⁶ that were obtained by the Thomas-Fermi method. Our calculated values differ from the data of Ref. 156 at P > 1000 GPa by no more than 30%.

2.4. Shock compression of substances

Let us study the compression of substances by shock waves using the equation that was obtained. Let the density, pressure, and internal energy of the substance ahead of the shock front be ρ_{00} , P_0 , and E_0 , and ρ , P_H , and Efollowing the front. The equation of the shock Hugoniot has the form

$$E - E_0 = \frac{P_{\rm H} + P_0}{2} \left(\frac{1}{\rho_{00}} - \frac{1}{\rho} \right). \tag{74}$$

Let us write the value of the energy E as the sum of cold E_c and thermal E_t components:

$$E = E_{\rm c} + E_{\rm t}, \quad E_{\rm t} = \frac{P_{\rm H} - P_{\rm c}}{\Gamma \rho}.$$
(75)

Here P_c is the value of the pressure at zero temperature, and Γ is the Grüneisen coefficient. In this case the relationship between the density and the pressure following the front of the shock wave is determined by the expression

$$P_{\rm H} = \{ P_{\rm c} - \Gamma \rho [E_{\rm c} - E_{\rm c}^{0} - E_{\rm t}^{0} - (P_{0}/2)(\rho_{00}^{-1} - \rho^{-1})] \} \\ \times [1 - (\Gamma \rho/2)(\rho_{00}^{-1} - \rho^{-1})]^{-1}.$$
(76)

For the case in which P_c and E_c are given by the relationships of (71), Eq. (76) is converted into the form

$$P_{\rm H} = [3B_0\{(\sigma^{5/3} - \sigma^{4/3}) - 1.5\Gamma\sigma[(\sigma^{1/3} - 1)^2 - (\sigma^{1/3} - 1)^2]\} + \Gamma\rho_0\sigma E_t^0 + (\Gamma P_0/2)(\sigma\sigma_1^{-1} - 1)] \times \{1 - (\Gamma/2)[(\sigma/\sigma_1) - 1]\}^{-1},$$

where $\sigma = \rho/\rho_0 _{\rm K}$, and $\sigma_1 = \rho_{00}/\rho_0 _{\rm K}$. The expression that we have presented determines the pressure in the first shock wave (in this case we have $P_c=0$, $E_c=0$), or the pressure in succeeding shock loads when the values of the density, pressure, and energy obtained in a preceding shock wave are taken as the initial values.

In calculations with $\sigma < 2.4$ in the compression following the shock wave, a value of the Grüneisen coefficient⁷³ was used that was obtained in the Dugdale–Macdonald approximation.⁶⁶ With the Grüneisen coefficient of Ref. 73 the limiting compression of the substance in the shock wave σ_{lim} is 3.5. Actually the compression of substances in a shock wave extends up to $\sigma = 5.^{63,157-159}$ Apparently the difference is explained by the electronic excitations of atoms in the solid upon strong heating in the shock wave. To describe the higher densities in a shock wave, for $\sigma > 2.4$ the following interpolation dependence was chosen for the Grüneisen coefficient:

$$\Gamma = \frac{\sigma^{1/3}}{\sigma^{1/3} - (2/3)} - 1.16. \tag{77}$$



FIG. 3. Values of the pressure on the shock Hugoniot of compact aluminum. *1*—calculation based on the model of the Bohr atom,³⁸ 2—calculation based on a modified Hartree–Fock–Slater model.

Using the obtained value of $P_{\rm H}$, we determine from Eq. (75) for a given ρ (or σ) the thermal energy following the front of the wave. From the formulation of the thermal energy in the Debye approximation

$$E_{t} = \frac{3RT}{A} \cdot 3\left(\frac{T}{T_{D}}\right)^{3} \int_{0}^{T_{D}/T} \frac{x^{3}dx}{e^{x} - 1}$$
(78)

we can determine from the value of E_t the temperature T following the front of the shock wave; here T_D is the Debye temperature, and R is the gas constant.

At high pressures very rich experimental information on compression by shock waves exists for aluminum. A detailed selection of these data is given in Ref. 74. Figure 3 compares the pressure on the shock Hugoniot of solid aluminum calculated by the method presented above (curve 1) with the experimental data^{59,61,157,158,164,178} and the calculated values of Ref. 74 (curve 2) obtained by a refined Hartree-Fock-Slater method. The lower curve in Fig. 3 corresponds to the calculated $P_c(\sigma)$ dependence by Eq. (71). The agreement with experiment is better on the average than in Ref. 74. The calculation describes well the measurements at moderate degrees of compression, for which elevated values were obtained in Ref. 74. At high compressions the calculation based on the Bohr model yields values of the pressure close to the experimental data of Refs. 157 and 178 and higher values than the measurements of Ref. 158 and the calculations of Ref. 74. At these compressions it passes closer to the results of the calculations by the quasiband model.⁷³ The calculation also describes the data of the measurements of Refs. 58 and 160 for porous aluminum.

Comparison of the calculated values of the pressures on the second shock Hugoniot in aluminum, performed from the state P=150 GPa, $\sigma=1.5$, with the experimental data of Ref. 161 shows that they agree well (to the accuracy that one can judge from the diagram in Ref. 161). We note also the good agreement of the temperature obtained in this calculation on the first shock Hugoniot in aluminum with the calculated data of Ref. 161. Analogous results are given by a comparison of the temperature $T_{\rm H}$ for sodium with the data of Ref. 162 and for molybdenum with the data of Ref. 163.

The study within the framework of a single numerical calculation of all stages of the action of a shock wave, beginning with compression and up to dispersal of the material strongly heated in the shock wave, requires application of a broad-range equation of state that is valid over a broad interval of variation of the parameters and which allows one to describe various physical effects. Such equations of state have been developed and rather widely applied in the practice of calculations.⁵⁷ These equations of state are unavoidably rather complex, containing a large number of adjustable parameters necessary to describe the various physical phenomena. Thus, in Ref. 56 to describe the processes of unloading after the action of a shock wave, the equation of state of copper and lead contains more than 40 parameters, of which 26 are adjustable parameters. Individual stages of the process (e.g., compression and not very deep unloading) can be studied by applying simpler equations of state, the advantage of which is their graphic character and clarity of the physical assumptions. We must discuss the equation of state (71) precisely from this standpoint.

2.5. On the energy of states of the atomic cell and phases of solids

The data on the compressibility of substances obtained both in static and in dynamic experiments yield rich information on the properties of substances. Jumps in the parameters and change of slope of the curve of the relationship of the pressure to the density (or to the specific volume) enable one to determine the phase transitions of substances to a new crystalline state. The most direct information on this question comes from x-ray structural studies of compressed substances (see, e.g., Ref. 65).

In dynamic experiments phase transitions are revealed by breaks in the shock Hugoniots. These phenomena are widely discussed in the scientific literature (we note the studies of L. V. Al'tshuler, in particular the reviews, Refs. 52, 53, and 78). There is a handbook on the phase diagrams of elements¹⁶⁶ and of compounds¹⁶⁷ at high pressure in which the results of both the static and dynamic experiments are generalized. A detailed analysis of the studies on structural and electronic phase transitions is contained in the review, Ref. 57.

References 168 and 169 call attention to the fact that the compressibility of substances is determined not only by their crystal structure, but also by their electronic structure. The idea of the possibility of phase transitions upon varying the distribution of the electrons over the shells is due to E. Fermi (see Ref. 170).

In Ref. 39, starting with concepts of the model of the Bohr atom, an attempt was made to determine the energy of the atomic states of the unit cell of solids on the basis of data on their compressibility, and also to correlate these data on the electronic structure for different phases of solids.

The expressions (69) and (71) for the elastic pressure in a solid are written both in terms of a macroscopic quantity (the bulk compression modulus B_0) and in terms of a microscopic quantity (the effective energy of the unit cell of the solid E_n):

$$P(\sigma) = 3B_0(\sigma^{5/3} - \sigma^{4/3}) = \frac{2E_n N_A \rho_n}{3A} (\sigma^{5/3} - \sigma^{4/3}).$$
(79)

Here A is the atomic mass, ρ_n is the density of the substance under equilibrium conditions, N_A is Avogadro's number, and $\sigma = \rho/\rho_n$. We can determine from Eq. (79) for a known value of the bulk compression modulus B_0 the effective energy of the state of the atomic cell contained within a solid:

$$E_n = \frac{9AB_0}{2N_{\rm A}\,\rho_n}.\tag{80}$$

If E_n is in electron volts, B_0 in GPa, and ρ_n in g/cm³, then we have

$$E_n = \frac{3B_0A}{64.3\rho_n}.$$

Values of the bulk compression modulus for simple substances (elements) under normal conditions are collected in Ref. 152. To obtain the values of B_0 at zero temperature, one must take account of the influence of thermal expansion upon heating. The decrease in the density of the substance upon heating leads, in line with (70), to a decrease in the bulk compression modulus ($\sigma < 1$). For a number of substances this decrease under normal conditions (T = 300 K) can be considerable (15–20%).

The values of B_0 and ρ_n for many elements and the values of the effective energy E_n of the atomic cell calculated for them by Eq. (80) when contained within a solid are given in Ref. 39.

The energy obtained by Eq. (80) amounts to the energy of the outer electron ring of the atom containing N equivalent electrons (in the Bohr model, revolving in one orbit and with identical velocities). This energy includes the sum of the kinetic energies of the electrons, their interaction energy with the atomic core and with one another, and also the energy of interaction with other atomic cells.

For the alkali metals one can treat this energy as the energy of the ground state of the free atom distorted by the influence of the adjacent atoms in the solid. In solid beryllium the obtained energy value almost coincides with the energy of the ground state of the free atom, but it is quite possible that in metallic beryllium the atomic cell is formed by a beryllium atom, not in the ground state $1s^22s^2$, but in the excited state $1s^22p^2$ (its energy for the free atom equals 20.5 eV). The situation is analogous for the other alkaline-earth elements, which have two electrons in the outer electron ring, for which one obtains a value of E_n close to the energy of the ground state of the free atom. For solid boron

the energy of the atomic cell $E_n = 30.7$ eV can be compared with the energy of the two outer electrons in the states $1s^22s2p^2$ of the free boron atom ($E_n = 29.9-24.5$ eV, depending on the type of term). For solid Al, Ga, In, and Tl; under normal conditions the energy of the atomic cell is also closer to the value for the two-electron configurations (e.g., $5s5p^2$ for indium).

The high energy of the atomic cell of carbon contained in diamond $E_n = 79$ eV favors a three-electron outer ring. The energy of the $1s^22s2p^3$ states of the free carbon atom lie in the range 79.3-70.4 eV, depending on the type of term. The energy of the carbon atom contained in graphite $E_n = 18$ eV can correspond to a one-electron outer configuration.

The carbon series is characterized by the presence of different crystal phases of any given element. The example of graphite and diamond shows that the different phases can differ not only in the arrangement of the atoms in the crystal lattice, but also in the differing electronic state of the atoms. As a rule, the atomic states of greater energy correspond to a larger density of the substance and a small compressibility (large value of the bulk modulus). The carbon series demonstrates also all the other possibilities. The high-pressure phase of germanium¹⁷¹ can be described by the parameters $\rho_n = 6.6 \text{ g/cm}^3$, $3B_0 = 320 \text{ GPa}$, corresponding to an energy of the atomic state $E_n = 54.9$ eV, close to the energy of the low-pressure phase $E_n = 52.2$ eV. In the given case the polymorphic modifications apparently differ only in the arrangement of the atoms in the crystal. The situation is the same in the high-pressure phase of silicon.⁴⁹ The parameters $\rho_n = 3.57$ g/cm³, $3B_0 = 440$ GPa that describe the pressure in this phase yield an energy of the atomic state $E_n = 54.0$ eV, which coincides with the energy for the low-pressure phase.

Gray tin, which has a lower density than white tin, at the same time has a large value of the bulk modulus and a twofold larger energy of the atomic state. While for the atomic cell of white tin we can expect a state with three equivalent outer electrons of the type $5s5p^3$ (its energy for the free atom equals $47.5-45.4 \text{ eV}^{107}$), for gray tin the four-electron configuration $5p^4$ is more suitable.

So-called isomorphous phase transitions are known in which a jumpwise change in volume occurs without change in the crystal structure of the substance (see, e.g., Ref. 64). These transitions are explained by the rearrangement of the electronic structure of the substance. It seems logically quite natural that the electronic phase transitions occur also with a simultaneous change in the crystal structure.

The polymorphic modifications of phosphorus are of interest. White phosphorus has perhaps the smallest energy of the state of the atomic cell of the solid ($E_n=3.6$ eV). This energy is comparable with the energy of the outer electron of the free phosphorus atom in the state $3s^23p^24s$ or $3s^23p^24p$ ($E_n=3-4$ eV). The small energy values, which correspond to one outer electron, and characteristic also of sulfur and selenium.

Among the rare-earth elements the two-electron configuration of the outer electron ring is rather definite for europium and ytterbium. For the rest of the lanthanides we can expect mainly states of the atomic cell with three equivalent outer electrons.

In the heavy metals (W, Ir, Re, etc.) the outer electron ring can contain up to five electrons, while the energy of the atomic cell can reach 150-170 eV.

For many elements and compounds phase transitions are manifested in shock-wave experiments in breaks in the shock Hugoniots.^{52,53,78} Parameters of the high-pressure phases determined by processing the shock Hugoniots are given in Ref. 39 (the high-pressure phases are marked with an asterisk). For antimony, bismuth, indium, and thallium the high-pressure phases have a density 20–25% higher than the density of the low-pressure phase, and an energy of the atomic state (100 eV) threefold greater, i.e., corresponding to a larger number of outer electrons. The highpressure phase observed in shock-wave experiments in germanium coincides with the phase determined under static pressure.¹⁷¹ The phase transitions in the rare-earth elements correspond to a strong change in the energy of the atomic state.

For complex multielectron atoms it is difficult to compare the states in the unit cell of the solid with the states of the free atom. One can compare the energy of the states in the solid with the energy of the ground state of the free atom, which equals the sum of the successive ionization potentials. In many cases the energy of the excited states (without change in the principal quantum number) does not strongly differ from the energy of the ground state (e.g., the states $1s^22s^2$ and $1s^22p^2$ of beryllium). The use of the energy of the atomic cell in the form of the sum of successive ionization potentials allows one to obtain better agreement with the experimental values of the bulk compression modulus¹⁵² than, e.g., a calculation by the pseudopotential method for the f-elements.¹⁷²

For compounds of the elements the unit cell of the solid can contain several atoms. A very simple calculation is possible in the case in which the dimension of the outer electron shell of one of the atoms or ions considerably exceeds the dimensions of the electron shells of the other atoms. The outer electron ring exists here in the electric field of the ionic residues of the other atoms of the cell, and it undergoes a certain influence of the adjacent cells. In this case the pressure is determined mainly by the compression of the electron ring having the greatest dimension.

In the alkali halides the transfer of charge from the atom of the alkali element to the halogen leads to the creation of the closed electronic configuration of an inert gas. In the cell of LiF a state is created here which, owing to the influence of the positive charge of the Li⁺ ion, is closer to the states of the neon atom than to the states of the negative ion F^- . Analogously in the oxides of the alkaline-earth elements a transfer occurs of two electrons from the alkaline-earth atom to the oxygen atom to form the same states of the noble gases. Electron transfer can occur from one atom, e.g., an alkaline-earth element, to two halogen atoms, as well as more complex cases of formation of an outer ring of electrons that determines the compressibility of the substance.

Silicon dioxide has a large number of crystalline mod-

ifications (polymorphic phases), among which the best known are quartz (α and β), coesite, and stishovite. We can consider that transfer of four electronic charges from the silicon atom to oxygen (two electrons each to each oxygen atom) results in neon-like states of the two oxygen ions, which exist in the electric field of the Si⁴⁺ ion. The strong difference in the energy of the atomic cell in the case of quartz, coesite, and stishovite can be treated as the consequence of formation in the unit cell of an outer electron ring of the neon-like ion containing a different number of electrons in each phase. The energy per neon-like atom of 20, 50, and 110 eV, respectively, in α -quartz, coesite, and stishovite corresponds to one, two, and three equivalent electrons in the outer electron ring.

Data on the compressibility of a large number of solid compounds of the elements (rocks) are collected in the handbook, Ref. 63. The values of the energy of state of the atomic cell of the solids obtained on the basis of these data [by using Eq. (80)] are presented in Ref. 39. For a number of compounds parameters were used that are given in the book, Ref. 173. The parameters of the substances were also refined from the data of other publications, e.g., the density of several compounds were taken from the handbook, Ref. 174.

One of the conclusions from the analysis that was performed³⁹ is the presence in many complex compounds of different polymorphic modifications, which as a rule differ also in the energy of the atomic state of the unit cell of the solid.

Attention is called to the fact that the oxides of many elements have an energy of the atomic state per oxygen atom of 100 eV, which is characteristic of stishovite (BeO, MgO, CaO, SnO₂, Al₂O₃, Fe₂O₃, UO₂, ZnO, etc.) For all these compounds one can expect the presence of neon-like states of the oxygen ions in the cell of the solid. The same energy value is observed in the high-pressure phases of CaF₂ and NaF, and a close-lying value in MgF₂. In these compounds one can expect neon-like states of the fluorine ions.

In addition to coesite, an energy of the atomic state of 50 eV (per neon-like ion) is found in the fluorides of the alkaline-earth elements (CaF₂, SrF₂, and BaF₂), in cuprite CuO, the high-pressure phase of lithium fluoride LiF, and in silicates (Fe₂SiO₄, ZrSiO₄, Mg₂SiO₄). The energy of the atomic cell of sulfates and carbonates corresponds to 30–35 eV per oxygen ion, which is close to the value for β -quartz.

The situation is analogous for the compounds of sulfur, which are characterized by an argon-like structure of the sulfur ion in the unit cell of the solid. The energy per sulfur ion contained in wurtzite (ZnS), marcasite (FeS₂), pyrite (FeS₂), stibnite (Sb₂S₃), and galena (PbS) amounts to 80 eV. The compounds Ag₂S, AgCl, and AgBr have an energy of 50 eV per argon-like ion, and the compounds CaCl₂, PbCl₂, and Bi₂S₃ have an energy of 30 eV.

At pressures up to 35–40 GPa the parameters of the equation of state of NaCl correspond to an energy of the atomic cell of 42 eV, while for P > 40 GPa they correspond to the high-pressure phase with $\rho_n = 3.24$ g/cm³, $E_n = 126$ eV. This phase describes the behavior of NaCl in shock-

wave experiments at P=40-90 GPa. The values of the pressure at T=0 calculated for this phase by Eq. (71) agree with an accuracy as good as 3-5% up to P=700 GPa with the pressure in the B2 structure of NaCl calculated in Ref. 175. An estimate is made in this study of the metallization of NaCl.

In the shock compression of andalusite (Al_2SiO_5) the part of the curve for compression values $\sigma > 1.3$ is described well by the parameters of kyanite having a porosity m = 1.2.

The parameters ρ_n and B_0 describe the compressibility of substances in the region of existence of the given phase state. To calculate the compressibility of a new phase one must replace the parameters in the equation of state (71). Some substances undergo phase transitions at low pressures (e.g., KCl at 2 GPa). Therefore the course of their compressibility is not determined by the value of the bulk compression modulus under normal conditions. The possibility of several phase transitions in lead with increasing pressure was noted in Ref. 161.

For many compounds, including rather complex ones, the obtained energies of the states of the atomic cell of the solid justify studying them starting with the electronic configuration of the inert gases. The realization in this configuration of states containing a different number of electrons in the outer ring, together with the crystal structure, determines the compressibility of the given substance in some phase or other.

Among the high-pressure phases determined from the results of shock-wave experiments, one cannot rule out the existence of metastable phases, which can be isolated after the action of the shock waves under the condition that the specimens are preserved after the explosion. The phases of silicon dioxide coesite and stishovite were discovered in a similar way in the early 60s in the sandstones of the Arizona meteor crater.

2.6. On the influence of electronic phases on the shock Hugoniots of substances

The dependence D(u) of the velocity of the shock wave D on the mass velocity u following the front of the wave for various substances has a varied character. It has been established experimentally that a linear relation D=a+su holds for many materials. However, a broad class of substances is characterized by a more complex, nonlinear dependence.⁵²⁻⁶¹ Deviations from linearity are usually attributed to porosity of the specimens, elastic waves, or phase transitions.^{52,58}

In Ref. 79 the behavior of substances upon pulsed shock loading is classified in terms of the slope of the D(u)curve. The first group contains substances for which the slope s=dD/du=1-1.3 is maintained over a considerable interval of u (i.e., the dependence is linear in character). For these substances the D(u) dependence characterizes the compression of the original phase (or the very same phase) throughout the interval of study of u. For s > 1.5convex Hugoniots are characteristic, with a decrease in slope at large u. Another group is formed by the alkalineearth and rare-earth elements, for which shock Hugoniots



FIG. 4. Dependence of the slope s=dD/du on the mass velocity u for different porosities m.

with breaks have been found. These breaks are explained by electronic phase transitions that arise upon compression in the shock wave.⁵³

Analysis of the data of both static and dynamic experiments shows that many materials can exist in different phase states.^{53,78} As was noted above (see Sec. 2.5), many phases of solids differ not only in crystal structure, but as a rule, in electronic structure. In Ref. 39 the energy of the outer electrons in the atomic cell of the solid, which are responsible for the compressibility of the substance, was determined for a number of substances in each phase state.

One can analyze the course of shock Hugoniots starting with the concept that different regions of the D(u)curve correspond to compression of different phases of the substance. Using the equation of state (71) and the Grüneisen coefficient of (73) and (77), one can obtain the dependence of the pressure $P_{\rm H}$ on the density ρ following the front of the shock wave. One determines the mass velocity from the found value of $P_{\rm H}$ on the basis of the laws of conservation of mass and momentum as the material passes through the front of the shock wave:

$$u = \left(\frac{P_{\rm H}(\sigma-1)}{\rho_{00}\sigma}\right)^{1/2}$$

together with the velocity of the shock wave $D = \sigma u/(\sigma - 1)$, and thus the calculated dependence D(u) $(\sigma = \rho/\rho_{00})$. Such an analysis has been performed in Ref. 84.

First of all we shall study by calculation the influence of the porosity of substances on the course of the shock Hugoniots. Figure 4 shows the dependence of the slope s=dD/du of the D(u) curve on the mass velocity u for substances having the parameters $\rho_n=2.76$ g/cm³, $B_0=120$ GPa for various values of the porosity $m=\rho_0/\rho_{00}$ (where ρ_{00} is the density of the material ahead of the front of the shock wave, and ρ_0 is the crystalline density at



FIG. 5. Dependence of the asymptotic slope \bar{s} (solid line) and the minimum slope (dashed line) on the porosity m of the specimens.

T=0). The calculated D(u) dependence in the general case is not linear, even for compact specimens. However, one can single out an interval of the mass velocity u in which we can consider the approximation of a linear dependence to be reasonable, in particular, upon allowing for the finite accuracy of the experimental quantities.

For porous specimens one notes the following rule: small values of u are characterized by a large slope s=dD/du, which decreases with increasing u to reach an almost constant value \bar{s} . A certain increase in the slope of D(u) is obtained in the calculation at large values of u for compact and porous specimens. Over a certain interval of u the D(u) dependence for a porous material can be approximately linear. This constant value of \bar{s} is increased with increasing porosity m of the material. The dependence of \bar{s} on m is shown in Fig. 5. A very similar dependence is obtained also for other parameters of the materials. A very great change in the asymptotic slope \bar{s} occurs at small values of the porosity m.

In the model being discussed the slope of the D(u)relationship for materials of low porosity, m = 1.01 - 1.05amounts to s = 1.1 - 1.2. At the same time for real materials it can lie in a rather broad range. This fact is explained as follows. First, as was already mentioned above, the compressed phase of the material following the front of the shock wave can differ from the original phase (i.e., have a different equilibrium density and a different bulk compression modulus). Here the compression of a phase with a crystal density larger than the original phase can be considered to be the compression of a porous material having its own nonlinear D(u) dependence and a larger value of the asymptotic slope \overline{s} . By choosing the magnitude of the porosity one can describe practically any observed slope of the D(u) curve, in particular in a narrow enough interval of the mass velocity u.

Another mechanism that alters to a certain extent the slope of the D(u) curve is thermal expansion of the material from T=0 to the temperature at which the experiment is performed. This thermal expansion has the result that the material under the experimental conditions must be treated as porous as compared with T=0. The equilibrium value of the radius of the atomic cell contained in a solid is

realized at zero temperature. Thermal motion displaces the system from a state of equilibrium. The density of the material under the external pressure P_0 is determined from the condition:

$$P_{\rm c} + P_{\rm t} = P_0$$
.

Usually under the experimental conditions we have $P_0=1$ atm $\langle P_c | = P_t$. Then, substituting the value of P_c from (71) and $P_t = \Gamma \rho E_t$, we obtain

$$3B_0(\sigma^{5/3}-\sigma^{4/3})+\Gamma\rho_n\sigma E_t=0.$$

For constant Γ we have .

$$\sigma^{1/3} = \frac{1}{2} \{ 1 + [1 - (4\Gamma \rho_n E_t / 3B_0)]^{1/2} \}.$$

For the case in which Γ depends on σ we can find a solution by iterations.

For many materials the decrease in density by thermal expansion from T = 0 K to normal experimental conditions does not exceed 1-2%. For the alkali metals Na, K, and Rb it amounts respectively to 4.8%, 5.5%, and 6.0%.¹⁷⁶ For a large coefficient of thermal expansion (e.g., for polyethylene) the change in density as compared with zero temperature can exceed 10%. Owing to this, the slope of D(u) in the asymptotic region can reach $\bar{s} = 1.25 - 1.30$.

When at a certain intensity of the shock wave a transition occurs to a new phase having an equilibrium crystal density greater than in the original phase, the D-u diagram has an initial linear region that corresponds to compression of the original phase, and then a branch of the curve convex upwards, which corresponds to compression of the porous new phase to which the transition occurs when acted on by the shock. The region of the D(u) curve corresponding to the high-pressure phase is described by a nonlinear dependence. That is, the change in slope of an individual region of D(u) cannot unambiguously serve as evidence of a change of the phase state. Under conditions of finite accuracy of the experimental data, the initial nonlinear region corresponding to the new phase and the region belonging to the original phase of the material can be interpolated by a linear dependence with a slope differing from the asymptotic slope of D(u) for the new phase. Here the break in D(u), which is often identified with a phase transition, can occur at parameters substantially different from the values of D and u for the actual phase transition.

Often one uses a quadratic interpolation of the experimental data $D(u) = a + su + hu^2$ with a negative coefficient *h*. This interpolation presupposes a linear dependence at small *u* and a deviation from linearity at large *u*. By calculation one obtains the opposite pattern; a clearly nonlinear dependence at small *u* and a dependence close to linear at large *u*. Therefore the quadratic interpolation, which can be chosen for a narrow interval of *u*, proves to be invalid for a broad interval of *u*.

Figure 6 shows the D(u) dependence for the elements Li, Be, and Na, which describe the compression of the original phase of the material throughout the range of mass velocities u. They are characterized by the small slope \bar{s}



FIG. 6. Shock Hugoniots of beryllium and sodium D(u) and lithium D(u) + 10. Dots—experiment, lines—calculation.⁸⁴

= 1.1-1.15. The calculated description⁸⁴ of the experimental points is rather good, including that for Be at high values of $u \ (u=25 \text{ km/s})$.¹⁷⁷

For most materials a better description of the experimental data at high pressures is obtained under the assumption that a phase different from the original one is being compressed. Figure 7 shows the D(u) dependence for aluminum. The dashed curve corresponds to the value of the bulk compression modulus at T=0 K of $B_0=78.6$ GPa,¹⁵³ obtained with correction of the experimental value for thermal expansion.¹⁵² The dot-dash curve corresponds to the parameters $\rho_n=2.76$ g/cm³ (m=1.02), $B_0=120$ GPa, and the solid line to $\rho_n=2.85$ g/cm³ (m=1.05), $B_0=78.6$ GPa does not describe the course of the D(u) dependence at any high pressures. A better description is obtained at the porosity m=1.05 and $\rho_n=2.85$ g/cm³, $B_0=135$ GPa.

For molybdenum and tungsten a description of the D(u) dependence over a broad interval of u is attained with the parameters $\rho_n = 11.06 \text{ g/cm}^3$ (m = 1.08), $B_0 = 445$ GPa for Mo and $\rho_n = 20.78 \text{ g/cm}^3$ (m = 1.08), $B_0 = 510$ GPa for W. The handbook values of B_0 ,¹⁵² which pertain to the original phase state, match experiment rather well up to pressures of 150 GPa. At larger compressions a calculation with these parameters yields pressure values too low. The elastic pressure in molybdenum and tungsten in the interval P = 150-400 GPa calculated with the parameters given above agrees to an accuracy of 1-2% with the results of Ref. 153. The calculated dependence for Mo and W is shown in Fig. 8. The dots indicate the experimental values from Refs. 58-61, 79, 177, and 178. Figure 8 also shows the calculated dependences and the experimental



FIG. 7. Shock Hugoniot of aluminum. Dots—experiment; dashed line calculation with $\rho_0 = 2.71$ g/cm³, $B_0 = 78.6$ GPa, m = 1.0; dot-dash line calculation with $\rho_0 = 2.76$ g/cm³, $B_0 = 120$ GPa, m = 1.02; solid line calculation with $\rho_0 = 2.85$ g/cm³, $B_0 = 135$ GPa, m = 1.05.

points¹⁷⁹ for porous Mo (m'=1.83) and W (m'=2.16), where m' is the porosity with respect to the density of the original phase. The calculated description of both the compact and the porous specimens of Mo and W is good. These



FIG. 8. Shock Hugoniots of molybdenum D(u) and tungsten D(u) + 10. Dots—experiment, solid line—calculation with the parameters of the high-pressure phase, dashed line—with the parameters of the original phase.



FIG. 9. Shock Hugoniots of copper D(u) and iron D(u) + 10. Dots—experiment, lines—calculation⁸⁴ with the parameters of the high-pressure phase.

elements, like the preceding ones (Li, Be, Na) belong to the first group of materials in the classification of Ref. 79.

The second group of elements,⁷⁹ which are characterized by a large slope of D(u) with a tendency for it to decrease at large values of u, includes, in particular, iron and copper. One can describe this dependence under the assumption that it corresponds to compression of a new phase having an equilibrium density ρ_n respectively 1.35 and 1.3 times larger than the density of the original phase for Fe and Cu. As is known, iron at a pressure of 13.5 GPa transforms to a new phase state. The high-pressure phase of iron that is described by experiments with shock waves at high pressures, however, differs from this phase $\rho_n = 10.6 \text{ g/cm}^3$, m = 1.35, $B_0 = 750 \text{ GPa}$. For the highpressure phase of copper we find $\rho_n = 11.6$ g/cm³, m = 1.30, $B_0 = 680$ GPa. The calculated dependences and the experimental points for compact specimens of Fe and Cu are shown in Fig. 9. The calculation rather closely describes the experimental data over a broad range of parameters. The normal isotherm of copper from a pressure of 95 GPa to 1000 GPa obtained by processing the shock Hugoniots is given in Ref. 161. The high-pressure phase of copper describes it at pressures greater than 220 GPa.

The third group⁷⁹ contains the elements characterized by a D(u) dependence with evident breaks. This picture of the *D*-u diagram is observed in practically all the rareearth elements, in the alkaline-earth elements, and in many compounds. A calculated description of the course of the shock Hugoniots using multiphase analysis is shown for



FIG. 10. Shock Hugoniots of bismuth D(u) and lanthanum D(u)+2. Dots—experiment, lines 1 and 3—calculation⁸⁴ with the parameters of the original phase, 2 and 4—with the parameters of the high-pressure phase.

such materials is shown in Fig. 10 for the examples of lanthanum and bismuth. The first, practically linear region pertains to compression of the original phase of the material. The change in slope of D(u) involves transition at the front of the shock wave to a new phase having a density greater than that of the original phase and with a greater energy of the electronic state. The nonlinear dependence characteristic of the porous high-pressure phase (with respect to its equilibrium density) describes the second region of the D(u) curve better than a rectilinear dependence with a slope differing from the slope of D(u) for the original phase.

The fact merits attention that a multiphase description of shock Hugoniots is obtained in many cases in the absence of any appreciable region of coexistence of phases. That is, when certain parameters of the shock wave are reached, a complete transition as though occurs to a new phase state (rearrangement of the electronic structure).

In 1964 S. B. Kormer and his associates,¹⁸⁰ in studying the shock compressibility of alkali-halide crystals, found for them an anomalous course of the shock Hugoniots in the high-pressure region. The studies in Ref. 180 were performed up to pressures P=400-500 GPa. One can offer an explanation of the results of these experiments starting with a multiphase description of the shock Hugoniots. Figure 11 shows the experimental D(u) points for NaCl, as well as the calculated curves for two phases of NaCl having the parameters given in Ref. 39. There is an initial linear





FIG. 11. Shock Hugoniot of NaCl D(u). Dots—experiment, line *I*—calculation⁸⁴ with the parameters of the original phase, 2—with the parameters of the high-pressure phase.

region of D(u) for the original phase (up to u=2.8 km/s). Then the course of the D(u) curve for compact specimens of NaCl corresponds to a porous high-pressure phase. Here the D(u) dependence for NaCl resembles the dependence for lanthanum and bismuth (see Fig. 10) and other materials.

The phase transition in NaCl at a pressure P > 30 GPa is well known.¹⁶⁷ However, when u > 7 km/s, the experimental points again fit the calculated shock Hugoniot of the original phase. We emphasize that this is not a linear continuation of the initial region, but a calculated dependence with the parameters ρ_n and B_0 of the first phase. An analogous pattern is observed¹⁸⁰ for KBr, LiF, and other compounds. Thus, at the points of the anomaly of the D(u) dependence found in Ref. 180 for the alkali-halide compounds, it is not a phase transition that occurs, but conversely, the phase transition disappears that is observed, e.g., in NaCl in the range of mass velocities u from 2.8 km/s to 7.0 cm/s. The material at larger pressures again is compressed like the original phase. The hypothesis¹⁷⁵ of a sharp decrease at the point of anomaly of the Grüneisen coefficient (down to 0.10) seems more artificial.

The energy of elastic compression,⁶⁷ being the energy of the outer electrons, must be supplemented by the energy of the inner electrons of the atomic core. This energy varies weakly upon compressing the atom, and is inessential in calculating the elastic pressure. However, it is essential in comparing the energy of different electronic phases of solids to determine the region of stability of each phase. Under conditions of equilibrium the phase must be realized that enables the least value of the free energy. If one knows

FIG. 12. Energy of the elementary atomic cell of NaCl (eV) as a function of the specific volume. Line *1*—calculation⁸⁴ with the parameters of the original phase, 2—with the parameters of the high-pressure phase.

the density at which the energies of both phases are the same, then in this case, knowing the equation of state of the phases in the form of (71), one can construct the course of the $E(\rho)$ curve and determine the region of existence of the phases.

For NaCl the point in the D-u diagram at which the D(u) curves of the two phases of the substance intersect corresponds to a density $\rho = 3.56$ g/cm³. If we assume that at this density the energies of the phases are equal, $E_{\rm I} = E_{\rm II}$, then we obtain for NaCl the E(V) diagram shown in Fig. 12. At the intersection point of the D(u)curves the pressures in the shock wave are equal in the first and second phases, and here the elastic pressure shows a break. Up to the point A ($\rho < 3.56$ g/cm³) the original phase I exists. In the density interval 3.56 g/cm³ $< \rho < 5.0$ g/cm³ phase II possesses a lower energy. However, owing to the sharper increase upon compression of the energy of phase II as compared with phase I, at a density $\rho = 5.0$ g/cm^3 (point B) E_I and E_{II} again intersect, and at larger pressures again phase I has the lower energy. This is observed in the experimental D(u) curves for NaCl, in which a transition to the new phase occurs in the interval 2.8 < u<7.0 km/s, while when u < 2.8 km/s or u > 7.0 km/s a state of the original phase is realized.

The dependence shown in Fig. 12 corresponds to the case of a high-pressure phase that cannot exist as a metastable phase upon removing the pressure. The condition for existence of a metastable phase is the presence on the $E_n(V)$ curve of two minima as, e.g., in carbon (the graphite and diamond phases). The calculated dependence of the elastic energy E(V) (Ref. 71) for the phases of carbon is shown in Fig. 13. Graphite has a lower density and an energy of the outer electrons lower in absolute magnitude



FIG. 13. Energy of the elementary atomic cell of carbon E as a function of the specific volume. Line *I*-calculation⁸⁴ for graphite, 2-for diamond.

than diamond, but a deeper minimum upon taking account of the inner electrons.

There is a great variety in the relative arrangement of the elastic-energy curves of different phases of materials. In the case in which the energy of the phases corresponds to the energy of a different number of outer electrons, the $E(\rho)$ curves intersect at two points or not at all. When the energy of the outer electrons is the same, one point of intersection exists. This is implied by the fact that the equality of the elastic energies of the phases yields the equation

$$(9B_{01}/\rho_{n1})[(\rho^{2/3}/2\rho_{n1}^{2/3}) - (\rho^{1/3}/\rho_{n1}^{1/3})] + E_{01}$$

= (9B_{02}/\rho_{n2})[(\rho^{2/3}/2\rho_{n2}^{2/3}) - (\rho^{1/3}/\rho_{n2}^{1/3})] + E_{02},

which is quadratic in $\rho^{1/3}$ for different energies of the inner electrons $E_{01} \neq E_{02}$, and linear when they are equal, i.e., when only the crystal structure is changed in the case of one particular electronic state of the atoms. Cases can also occur in which both intersection points lie on the left-hand branch of the $E(\rho)$ curve, which corresponds to stretching of the specimen. Apparently a phase transition is possible both in compression and in stretch of specimens.

Let us trace by calculation the course of the D(u)dependence in the case in which a phase is formed in the process of phase transition at the front of the shock wave that has an initial crystal density smaller than the initial density of the original phase. In the calculation one obtains the D(u) dependence in the form of a curve convex downward, in contrast to the shock Hugoniots of porous materials, which have an upward convexity. Among the experimental data of Refs. 59 and 61 it is easy to find D(u)dependences having this form, e.g., B, BeO, and SiC. Such an unusual picture of the D-u diagram with decreasing D



₽, km/ s

16

15

14

13

at low values of u was demonstrated most clearly for aluminum nitride AlN in Ref. 181. Let us study by calculation

km/s

the change in the course of the shock Hugoniots for such a phase transition upon varying the initial density of the original phase. At a density of the original phase equal to the density of the compact material of this phase, there is a linear region of D(u) corresponding to compression of the original phase, and a nonlinear dependency with downward convexity of the curve that describes the compression of a "loose" phase, i.e., having a smaller equilibrium density than the original phase. If we take the density of the original phase (porous) to be equal to the crystal density of the "loose phase", then in calculation we have a nonlinear initial region of the D(u) dependence with upward convexity of the curve, and after phase transition a linear region of D(u) corresponding to the new phase with its own equilibrium initial density. For even greater porosity one obtains a D(u) dependence characteristic of ordinary porous specimens.

A pattern close to that described is shown in Fig. 14 with the example of BeO having densities of 2.99, 2.86, and 2.45 g/cm³. Figure 14 shows the experimental data of Ref. 182 and calculation with the parameters of the equation of state of BeO: $\rho_n = 2.93 \text{ g/cm}^3$, $B_0 = 207 \text{ GPa}$.

CONCLUSION

The presented treatment shows that the model of the Bohr atom, starting with circular orbits of the electrons with corresponding quantization rules, allows one, with a

semiempirical refinement of it, to describe quantitatively a broad set of physical phenomena in atoms, molecules, and solids.

Thus one can obtain the energy values of different states of free multielectron, multiply charged ions with an accuracy sufficient for spectroscopy. An analytic expression was obtained for the energy of the ground state of helium-like ions that takes account of relativistic effects and describes experiment to high accuracy, and which can be used for ions with a large nuclear charge Z.

The energies of different states of He-, Li-, Be-, and B-like ions have been calculated, which have been compared with the experimental data and the results of exact quantum-mechanical calculations. Fine-splitting spacings of the energy of these states were obtained that match well the experimental values. Attention is called to the influence of the outer electrons on the magnitude of the fine splitting of the energy of the states of the inner electrons. For $1s^22lnl'$, $1s^22l^2nl'$, and 1s2lnl' states, with increasing degree of excitation of the outer electron (increasing n), the energy difference between the extreme components of the multiplet increases and approaches the value for the ion in which this outer electron is absent.

By using the model of the Bohr atom it has been possible to obtain analytic expressions for the energy of highly excited (Rydberg) states of helium-like and lithium-like ions and analytic dependences on Z of the quantum defect and on Z and n of the screening coefficient for the same ions for states with a given l. Here one obtains with sufficient accuracy the energies of transitions between states having the same n.

The method developed for atoms and atomic ions was applied to calculate the energy of the excited electronic states of the hydrogen molecule. Comparison of the experimental ionization potentials of excited states with those calculated in this way enables one to establish the correspondence of energy levels in the molecular classification and the energy levels of one-electron excited states of the hydrogen molecule with the classification of the analogous states of the helium atom. One can describe the energy of the electronic excited states of other molecules on the basis of the classification of the energy levels of atoms isoelectronic or isosteric with them.

The application of the model of the Bohr atom to calculate the energy levels of nonequilibrium atomic systems at constant atomic volume has been rather successful. This model was used to calculate the energy of the compressed atom and to obtain on its basis a semiempirical equation of state of solids. Analytic expressions were obtained based on this model for the dependence of the elastic energy and the elastic pressure on the degree of compression, which describe experiment well for many substances.

The method being used enables one to associate the change in energy on compressing a material with the equilibrium energy of the outer electrons in the atomic cell of the solid and makes it possible to determine the effective energy of the atomic state from the known value of the bulk compression modulus. By this method the effective energy of the elementary atomic cells of solids have been determined for more than 100 elements and compounds. The results of these calculations call attention to the fact that the different phases of solids differ not only in crystal structure, but also, as a rule, in electronic structure (effective energy of the atomic cell of the solid).

In many cases the model of matter being discussed yields an explanation of the complex behavior of shock Hugoniots D(u), starting with the concept that the different regions of this curve correspond to compression of different phases (including electronic ones) of the material. It proved possible to identify a clearly nonlinear region of the D(u) dependence with the compression of a phase of the material differing from the original (i.e., having a different equilibrium crystal density and a different bulk compression modulus).

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