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COMPACT MOLECULE OF BERYLLIUM

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The interaction potential for beryllium atoms is calculated using the Ritz variational method with molecular wave functions as trial functions. The results of calculations for Be_2 *molecules in the* $^1\Sigma_g^+$ *state, which from the well-known data is considered ground, coincide with the results of previous studies. Similar calculations for the* $^3\Sigma_u^+$ *state show that the minimum energy for this state is reached at shorter internuclear distance and is lower than that for the* $^1\Sigma_g^+$ *state.*

Introduction. Examining the dense states of materials is a fundamental problem of modern physics. Interest in this problem is motivated by the possibility of designing new materials and chemical compounds. This can be achieved not only by slow high-pressure loading but also by dynamic compression methods (impact, cavitation, etc.), which are less expensive but are accompanied by a sharp rise in temperature and ionization of the material.

Loading of crystalline materials by high-pressure presses leads to the occurrence of phase transitions accompanied by a jumpwise decrease in volume. Most of these transitions are explained by a change of the type of crystal lattice, but for some of them this explanation is inapplicable; in this case, the electron configuration changes with increase in the external pressure. Thus, the phase transition of the first kind in cesium at a pressure of 45 kbar, which is accompanied by a 5.6% jumpwise decrease in volume, was explained by transition of the valence electron of cesium from the $6s$ state to the $5d$ state [1]. Alekseev and Arkhipov [2] predicted theoretically the possibility of the $5s$–$4d$ electron transition for rubidium, which was later detected experimentally by Stager and Drickamer [3]. Similar transitions were also observed for other substances. The most marked decrease in volume (by 16.5%) occurs for cerium at a pressure of 15 kbar [4].

An analysis of [1–4] shows that a decrease in the interatomic distance in a solid can result in the formation of new stable electron configurations that fix the diminished distance by changing the volume of the solid. It can be assumed, however, that denser states also form in simple structures, for example, diatomic molecules. If the electronic structure of a molecule is sufficiently complex, then a decrease in the internuclear distance relative to the equilibrium position (this change implies a strong external action) can lead to the formation of an electron configuration that stabilizes the more compact state of the molecule. The present paper is devoted to a study of this problem. To simplify the calculations, we used a symmetric diatomic molecule. The possibility of formation of compact states was analyzed for molecules starting with hydrogen. This possibility was detected for the Be_2 molecule, which was chosen as the object of investigation.

The electron configurations of diatomic molecules were calculated using the variational method (see, for example, [5]). As the trial wave functions we used molecular wave functions that correspond to the geometry most closely, i.e., exact solutions of the problem of behavior of an electron in the field of two attractive centers.

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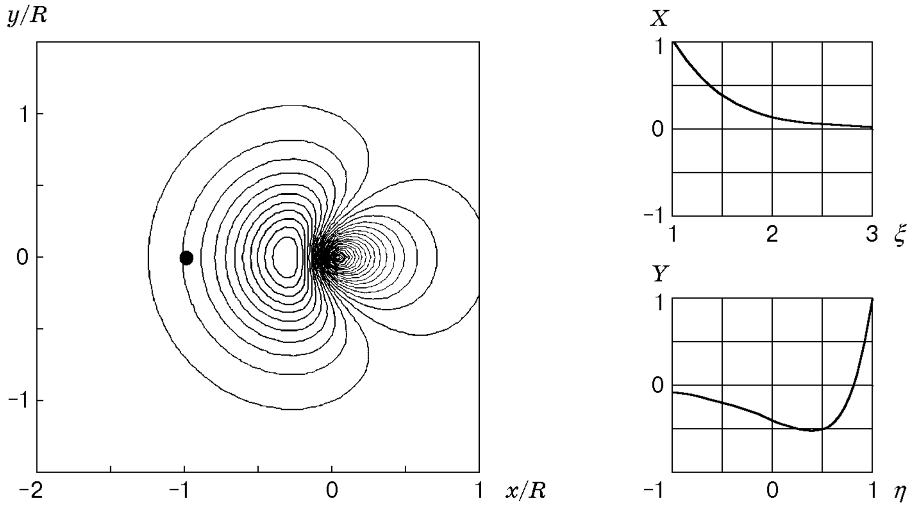

Fig. 1. Topogram of the $2p\sigma$ state with charges $\alpha = 3$ and $\beta = 0$ (point indicates the position of the zero charge).

1. Molecular Wave Functions. The problem of finding the wave function of an electron in the field of two nuclei with charges α and β and internuclear distance R was solved exactly (see, e.g., [6]). The wave functions of the solution of this problem

$$\psi_{n_1 n_2 m} = X_{n_1}(\xi) Y_{n_2}(\eta)\, \mathrm{e}^{im\varphi} \tag{1}$$

form a complete orthogonal system of functions in a three-dimensional coordinate space (ξ, η, and φ are elliptic coordinates). The set of elliptic quantum numbers (n, n_2, and m) completely determines a wave function in elliptic coordinates [6, 7]. Here $n = n_1 + n_2 + m + 1$ is the principal quantum number, m is the projection of the orbital moment, and n_1 and n_2 are elliptic quantum numbers. In the standard notation of electronic terms, the quantum numbers of the projection of the orbital moment $m = 0, 1, 2, \ldots$ are denoted by Greek letters σ, π, $\delta, \ldots$, and the values of $n_2 + m = 0, 1, 2, \ldots$ are denoted by Latin letters s, p, $d, \ldots$. For example, the $2p\pi$ term corresponds to values $n = 2$, $n_2 = 0$, and $m = 1$.

Figure 1 shows a topogram of the wave function $2p\sigma$ for the case where one of the charges is equal to zero (distances are expressed in terms of R). In this case, the energy of the state is equal to the energy of the state of a hydrogen-like atom with nuclear charge α and principal quantum number n:

$$E_{n_1 n_2 m} = -\frac{\alpha^2}{n^2}\ \mathrm{Ry}.$$

Here the Rydberg number Ry = 13.6 eV is the ionization potential for hydrogen. In this case, a molecular wave function can be expressed in terms of a superposition of spherical wave functions with the same principal quantum number, and, vice versa, a spherical wave function can be expressed in terms of a superposition of molecular functions. Thus, with accuracy to normalization, the spherical wave function $2p_0$[1] is the simple difference of the molecular wave functions of the $2s\sigma$ and $2p\sigma$ states:

$$\psi_{2p_0} = \psi_{2s\sigma} - \psi_{2p\sigma}. \tag{2}$$

Because of geometrical features, the spherical wave function $2s_0$ is expressed in terms of molecular functions in a somewhat more complex form:

$$\psi_{2s_0} = \psi_{2s\sigma} + k\psi_{2p\sigma}, \tag{3}$$

where k is a geometrical coefficient. We note that the spherical wave function of the $1s_0$ state coincides with the molecular wave function $1s\sigma$, and the function of the $2p_1$ state coincides with the function of the $2p\pi$ state. The states of atoms are usually characterized by the value of the orbital moment. The atomic states are described by spherical wave functions, and molecular wave functions do not have a definite value of the orbital moment.

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[1] In the standard notation of the hydrogen-like state, the number 2 corresponds to the main quantum number and p corresponds to orbital moment 1; the subscript 0 indicates the projection of the orbital moment.

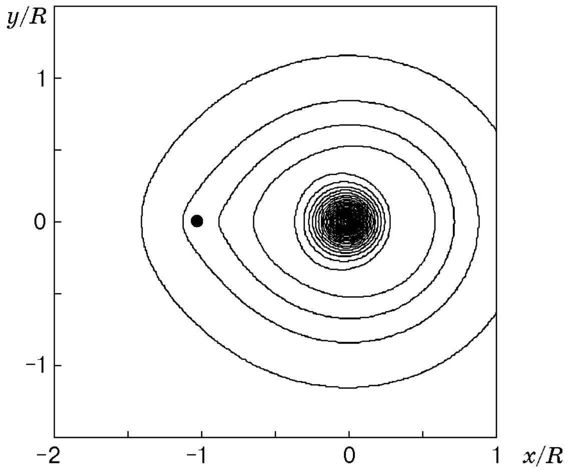

Fig. 2

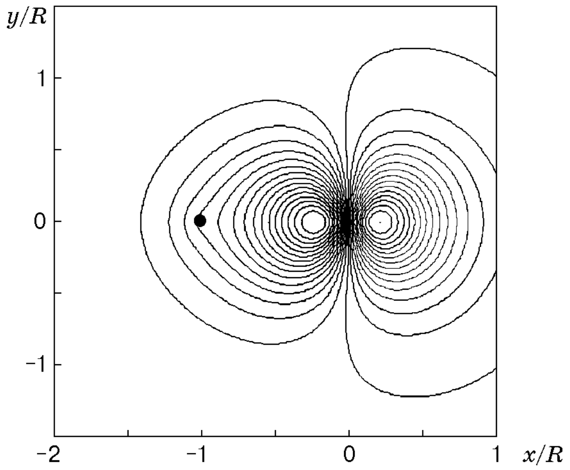

Fig. 3

Fig. 2. Topogram of the $2s_0$ state with charges $\alpha = 3$ and $\beta = 0.5$ (point indicates the position of the additional charge).

Fig. 3. Topogram of the $2p_0$ state with charges $\alpha = 3$ and $\beta = 0.5$ (point indicates the position of the additional charge).

In the presence of a second charge, the spherical molecular wave functions (2) and (3) are no longer exact solutions of the Schrödinger equation because of the action of the additional charge (in Figs. 2 and 3, this charge is indicated by a point). The variation of the wave function is similar to the variation of the spherical wave function of the atom with approach of the other atom. Therefore, the use of spherical molecular functions as the trial functions in the variational method simplifies the calculations considerably.

2. Electron Configurations of Symmetric Molecules. The electron configurations are calculated by the variational method (see, e.g., [5, 8]). As the trial function we use the symmetric electron wave function

$$\Psi = \begin{vmatrix} u_1(1) & u_1(2) & \ldots & u_1(N) \\ u_2(1) & u_2(2) & \ldots & u_2(N) \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ u_N(1) & u_N(2) & \ldots & u_N(N) \end{vmatrix}, \tag{4}$$

where $u_i(j) = \psi_i^{\alpha_i\beta_i}(\boldsymbol{r}_j)\chi(\sigma_j)$ is a one-particle electron wave function, which consists of coordinate and spin parts. As the coordinate functions we use the molecular functions (1) and/or the spherical molecular functions (2) and (3). In energy calculations, the effective charges α_i and β_i are variational parameters.

With allowance for the symmetry of the wave function (4), the total energy of a diatomic molecule with nuclear charges Z_α and Z_β is calculated from the formula

$$\langle\hat{H}\rangle = \frac{Z_\alpha Z_\beta}{R} + \left\langle \sum_i \Big(-\frac{1}{2}\,\Delta_i - \frac{Z_\alpha}{|\boldsymbol{r}_\alpha - \boldsymbol{r}_i|} - \frac{Z_\beta}{|\boldsymbol{r}_\beta - \boldsymbol{r}_i|} \Big) + \sum_{ij} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right\rangle$$

$$= \frac{Z_\alpha Z_\beta}{R} + N\Big\langle -\frac{1}{2}\,\Delta_1 - \frac{Z_\alpha}{|\boldsymbol{r}_\alpha - \boldsymbol{r}_1|} - \frac{Z_\beta}{|\boldsymbol{r}_\beta - \boldsymbol{r}_1|} \Big\rangle + \frac{N(N-1)}{2}\Big\langle \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Big\rangle,$$

where $N = Z_\alpha + Z_\beta$ is the total number of electrons. The calculation of the Laplacian is simplified by introduction of the operators

$$\hat{\Lambda} = -\frac{1}{2}\,\Delta - \frac{\alpha}{|\boldsymbol{r}_\alpha - \boldsymbol{r}|} - \frac{\beta}{|\boldsymbol{r}_\beta - \boldsymbol{r}|}, \quad \hat{U} = \frac{Z_\alpha - \alpha}{|\boldsymbol{r}_\alpha - \boldsymbol{r}|} + \frac{Z_\beta - \beta}{|\boldsymbol{r}_\beta - \boldsymbol{r}|},$$

$$\hat{\Lambda} - \hat{U} = -\frac{1}{2}\Delta - \frac{Z_\alpha}{|\boldsymbol{r}_\alpha - \boldsymbol{r}|} - \frac{Z_\beta}{|\boldsymbol{r}_\beta - \boldsymbol{r}|}, \quad \hat{\Lambda}\psi_{nn_2m}^{\alpha\beta}(\boldsymbol{r}) = E_{nn_2m}^{\alpha\beta}\psi_{nn_2m}^{\alpha\beta}(\boldsymbol{r}),$$

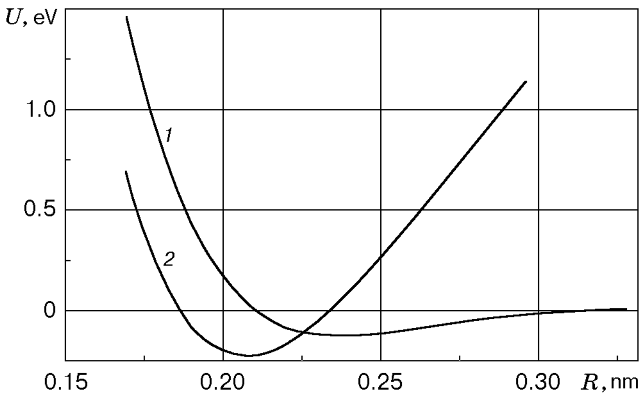

Fig. 4. Interaction potential for beryllium atoms in the ${}^1\Sigma_g^+$ (curve 1) and ${}^3\Sigma_u^+$ states (curve 2).

where $E^{\alpha\beta}_{nn_2m}$ is the natural energy of the molecular wave function $\psi^{\alpha\beta}_{nn_2m}$. If the one-particle functions are only molecular functions, the total energy is determined from the formula

$$\langle \hat{H} \rangle = \frac{Z_\alpha Z_\beta}{R} + \sum_{nn_2m} E^{\alpha\beta}_{nn_2m} - N\langle \hat{U} \rangle + \frac{N(N-1)}{2} \Big\langle \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \Big\rangle.$$

Minimizing the total energy by variation of the parameters α_i and β_i, we obtain the required electron configuration.

3. Ground State of Molecular Beryllium. In the calculation of the Be$_2 X^1\Sigma_g^+$ ground state, the wave function (4) can be written as

$$\begin{gathered}\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4, \boldsymbol{r}_5, \boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8) = [(\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)\Phi'(\boldsymbol{r}_5, \boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8) \\ + \Phi'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)\Phi(\boldsymbol{r}_5, \boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8))(1\!\uparrow 2\!\uparrow 3\!\uparrow 4\!\uparrow\ \ 5\!\downarrow 6\!\downarrow 7\!\downarrow 8\!\downarrow -1\!\downarrow 2\!\downarrow 3\!\downarrow 4\!\downarrow\ \ 5\!\uparrow 6\!\uparrow 7\!\uparrow 8\!\uparrow)] \\ - [(\Phi(\boldsymbol{r}_5, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)\Phi'(\boldsymbol{r}_1, \boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8) + \Phi'(\boldsymbol{r}_5, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)\Phi(\boldsymbol{r}_1, \boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8)) \\ \times (5\!\uparrow 2\!\uparrow 3\!\uparrow 4\!\uparrow\ \ 1\!\downarrow 6\!\downarrow 7\!\downarrow 8\!\downarrow -5\!\downarrow 2\!\downarrow 3\!\downarrow 4\!\downarrow\ \ 1\!\uparrow 6\!\uparrow 7\!\uparrow 8\!\uparrow)] + \dots\ .\end{gathered} \tag{5}$$

Here $1\!\uparrow$ indicates the spin part of the electron wave function. The wave functions $\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$ for electrons in the same spin state are antisymmetric about any permutation of the electron coordinates:

$$\Psi = \begin{vmatrix} \psi_1(\boldsymbol{r}_1) & \psi_1(\boldsymbol{r}_2) & \psi_1(\boldsymbol{r}_3) & \psi_1(\boldsymbol{r}_4) \\ \psi_2(\boldsymbol{r}_1) & \psi_2(\boldsymbol{r}_2) & \psi_2(\boldsymbol{r}_3) & \psi_2(\boldsymbol{r}_4) \\ \psi_3(\boldsymbol{r}_1) & \psi_3(\boldsymbol{r}_2) & \psi_3(\boldsymbol{r}_3) & \psi_3(\boldsymbol{r}_4) \\ \psi_4(\boldsymbol{r}_1) & \psi_4(\boldsymbol{r}_2) & \psi_4(\boldsymbol{r}_3) & \psi_4(\boldsymbol{r}_4) \end{vmatrix}. \tag{6}$$

The coordinate parts of the one-particle wave functions $\psi_1(\boldsymbol{r}_i)$ and $\psi_2(\boldsymbol{r}_i)$ correspond to the lower states of the electrons localized around the left and right nuclei. The functions $\psi_3(\boldsymbol{r}_i)$ and $\psi_4(\boldsymbol{r}_i)$ correspond to the upper states of the electrons. The function $\Phi'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$ of the other spin state is the coordinate inversion of the function $\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$:

$$\Phi'(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4) = \Phi(-\boldsymbol{r}_1, -\boldsymbol{r}_2, -\boldsymbol{r}_3, -\boldsymbol{r}_4).$$

With this inversion of the function, $\psi_1(\boldsymbol{r}_i)$ and $\psi_2(\boldsymbol{r}_i)$ are expressed in terms of one another (the lower shell is completely occupied).

In calculating the total energy, it suffices to use the first term of the wave function (5) because the spin parts of all terms of the sum are orthogonal to one another and the coordinate parts make, by virtue of symmetry, the same contribution to the energy.

The calculations show that the Be$_2\,{}^1\Sigma_g^+$ ground state corresponds to the $(2s_0)^2(2p_0)^2(1s\sigma)^4$ electron configuration [$2s_0$ and $2p_0$ are the states computed from formulas (2) and (3)]. Minimization of the total energy by selection of three pairs of the parameters α_i and β_i for each distance R allows us to construct the interaction potential for beryllium atoms (Fig. 4). As the zero of the potential we use the asymptotic (for large R) expression for the total energy of the atoms in the configuration $(2s_0)^4(1s\sigma)^4$, which, at $R = \infty$, corresponds to two noninteracting atoms.

The minimum of the potential is reached at an internuclear distance of $r_e = (0.242 \pm 0.004)$ nm and is equal to $D_e = (0.123 \pm 0.015)$ eV.

The $X^1\Sigma_g^+$ state for the beryllium molecule was calculated in [9–11], where this state was referred to as the ground state. The interatomic distances r_e obtained in those studies vary from 0.244 nm [11] to 0.245 nm [9], and the absolute value of D_e varies from 790 cm^{-1} (0.098 eV) [9] to 944 cm^{-1} (0.117 eV) [11]. A more recent work [11] contains a detailed analysis of the computational methods used, and the results obtained there seem to be the most reliable (the vibration spectra calculated in that work coincide with experimental spectra with an error of less than 3%). According to [11], the calculated minimum of the energy is equal to $D_e = (0.117 \pm 0.003)$ eV.

4. Compact State of Molecular Beryllium. The wave function of the $X^3\Sigma_u^+$ state with spin 1 is evaluated similarly. Since the total spin of the system is not equal to zero, there is no symmetry about the inversion of all spins:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4, \boldsymbol{r}_5, \boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8) = \Upsilon(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4, \boldsymbol{r}_5)\Upsilon'(\boldsymbol{r}_6, \boldsymbol{r}_7, \boldsymbol{r}_8) 1\!\uparrow 2\!\uparrow 3\!\uparrow 4\!\uparrow 5\!\uparrow\ \ 6\!\downarrow 7\!\downarrow 8\!\downarrow$$

$$- \Upsilon(\boldsymbol{r}_6, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4, \boldsymbol{r}_5)\Upsilon'(\boldsymbol{r}_1, \boldsymbol{r}_7, \boldsymbol{r}_8) 6\!\uparrow 2\!\uparrow 3\!\uparrow 4\!\uparrow 5\!\uparrow\ \ 1\!\downarrow 7\!\downarrow 8\!\downarrow + \ldots\ .$$

The functions Υ and Υ' are antisymmetric about permutation of any pair of vectors and are written in the form of determinants similar to (6).

The interaction potential for the atoms is shown in Fig. 4. At the minimum of the potential, the internuclear distance is equal to $r_e = 0.208$ nm, which is 14% smaller than that in the ground state. The minimum of the potential of the compact state is 0.1 eV lower than that of the ground state. As $R \to \infty$, the right branch of the compact state tends to the energy of a metastable beryllium atom, 2.725 eV.

5. Discussion of Results. The compact state of molecular beryllium $^3\Sigma_u^+$ can be obtained when a beryllium atom in the ground state approaches a metastable atom with spin 1. The latter can be produced by recombination of a beryllium plasma. Thus, a compact molecule can be formed only after passage of beryllium-containing material through the plasma state. An increase in the plasma density increases the yield of compact beryllium.

Although the energies of compact and ordinary beryllium are close, the binding energy of compact beryllium is 2.94 eV, which is determined by the energy of the metastable state[2] of Be atoms with spin 1, whereas the binding energy of an ordinary beryllium molecule is 0.12 eV. This implies that compact beryllium is much more stable against direct thermal decomposition.

The chemical properties of compact beryllium should differ markedly from those of ordinary beryllium because the electrons of the outer shell of a compact molecule are closer to the two nuclei and, thus, compensate for their repulsion.

The formation of compact beryllium is related to the inversion of the spin of one of the σ electrons of an ordinary beryllium molecule. A similar situation is also possible for other molecules, including nonhomonuclear ones. The formation of a chemical bond with a new structure, as in compact beryllium, can lead not only to a decrease but also to an increase in the energy of molecules. In this case, long-lived metastable molecules with unique chemical properties are formed.

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[2] Bond rupture in compact beryllium results in the formation of two atoms in the ground and metastable states.

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