

# Interatomic interaction within a $^4\text{He}$ – $^4\text{He}$ dimer with mobile nuclei

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## ABSTRACT

Schrodinger equation for system of two mobile spinless nucleus with  $Z_0 = 2$  and four electrons ( $^4\text{He}_2$ -dimer) has been solved in the framework of exact diagonalization approach. The spectrum has been obtained with basis of 1134 functions built as direct product of one-particle hydrogen-like functions which are solutions of the exactly solved Sturm-Liouville problem. The asymptotic (Van der Waals) behavior of interaction between two  $^4\text{He}$  atoms in the limit  $R_0 \rightarrow \infty$  has been analyzed and discussed. The contribution to the interaction energy from four electronic spins on the  $^4\text{He}$ – $^4\text{He}$  bond has been calculated the exact diagonalization procedure.

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## 1. INTRODUCTION

The difference between the two isotopes of helium is only the nuclear spin of  $^3\text{He}$ , but they demonstrate the surprising dissimilarity in their physical properties. Whereas  $^3\text{He}$  remains simple liquid up to very low temperatures, the  $^4\text{He}$  undergoes the  $\lambda$ -transition to He II phase at saturated vapor pressure. This phase provides several special effects (superfluidity, second, third, etc. sounds, vortices, and others). Last decade the microwave response of He II was discovered in a series of works.<sup>1–8</sup> The most essential feature of this response is a temperature dependent absorption line whose position on the frequency axis reproduces exactly the temperature and pressure dependence<sup>9</sup> of the roton gap discovered from neutron measurements.<sup>1,7,8</sup> When saying “roton” one must mean probable some special degree of freedom possesses a property of angular momentum. On the other hand, the “roton” branch is the direct prolongation of the phonon  $^4\text{He}$  spectrum beyond the roton minimum point into region<sup>9</sup> of small wave vectors  $k > k_{\min} \sim 2 \text{ \AA}^{-1}$ . Note, that  $k_{\min} = 2 \pi / \lambda_{\min}$  corresponds to wavelength  $\lambda_{\min} \sim 3 \text{ \AA}$  just comparable to interatomic distances  $a \sim 3 \text{ \AA}$  in condensed helium phases. The  $k_{\min}$  increases with pressure,<sup>9</sup> so that with pressure the  $\lambda_{\min}$  becomes smaller (it corresponds to compression of the medium). Thus, if we consider spectra obtained with neutron diffraction then we can conclude that the branch at  $k > 2 \pi / \lambda_{\min}$  corresponds to wavelength

$\lambda < \lambda_{\min} \sim a$  and, hence, to the scattering by the objects arranged on the sublattice scale. The only objects of such kind could be spins.

To describe the behavior of the spin subsystem we have to calculate properly the matrix elements of spin-spin and spin-orbital interaction (it is noticeable, that as law of roton-roton interaction in Ref. 9 has been given just the exact formula for interaction energy of two magnetic moments with coordinates  $\mathbf{r}_\alpha, \mathbf{r}_\beta$ , see Sec. 5 of the cited paper). The mentioned matrix elements depend on spatial variables, and the calculation needs to know the solution of the corresponding Schrodinger (or Pauli) equation, and this part of the problem is far from rigorous preparation. In the paper<sup>10</sup> we solved the Schrodinger equation within Born-Oppenheimer-Heitler-London approach<sup>11,12</sup> (four spinless electrons moving in the Coulomb field of two immobile nuclei with  $Z_0 = 2$  spaced at fixed distance  $R_0$ ), taken into account only pair exchange within the four-spin subsystem on the He–He bond. Here we propose the further modification of the solution, taken in addition into account the rotating degrees of the nuclear dumbbell, and four-spin antiferromagnetic exchange in the spin subsystem on the interatomic bond.

The theory of intermolecular forces was discussed and interpreted fifty years ago in fundamental book of Margenau and Kestner.<sup>13</sup> The only matter which remains actual since that time is rigorous quantum-mechanical treatment of the problem based on

the exact solution of a linear Schrodinger equation even if for a system of a few interacting nuclei and electrons. Using exact diagonalization approach, in Ref. 14 we built the solution for spinless helium atom with two electrons in a Coulomb central field (the quite similar method was used in Ref. 15). In Ref. 10 the study was extended on hydrogen-hydrogen and helium-helium pair interaction within Born-Oppenheimer-Heitler-London approximation. Here we obtain solution for helium-helium dimer with mobile nuclei (Sec. 3), i.e., we develop the exact diagonalization procedure for the system of two nucleus with  $Z=+2$  and four electrons (fifteen spatial variables). The contribution from the four electronic spins have been calculated and discussed (Subsection. 6.3).

## 2. TWO INTERACTING HELIUM ATOMS (HELIUM DIMER)

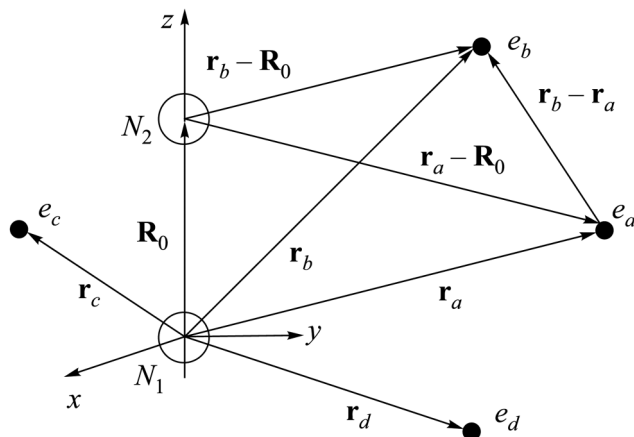
We consider the  $^4\text{He}_2$ -dimer as the system of six charged particles:<sup>10</sup> two nuclei with the positive charges  $Z_1 = Z_2 = Z_0 = +2$  and coordinates  $\mathbf{R}_1 = 0$ ,

$$\mathbf{R}_2 = R_0(\sin \Theta_0 \cos \Phi_0, \sin \Theta_0 \sin \Phi_0, \cos \Theta_0) = \mathbf{R}_0,$$

as well as four electrons with charges  $Z_a = Z_b = Z_c = Z_d = -1$  and coordinates  $\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d$  respectively. Here and below the Hartree atomic units have been used. Figure 1 shows the configuration of the system (for simplicity, only electrons  $a$  and  $b$  are marked, and the internuclear distance  $\mathbf{R}_0$  has been combined with  $z$ -axis).

The Hamiltonian of the problem has the form<sup>10</sup>

$$\begin{aligned} \hat{H}_{\text{tot}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = & -\frac{1}{2\mu} \Delta^{(\text{nuc})}(\mathbf{R}_0) + \frac{Z_0^2}{R_0} + H^{(e)}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) \\ & + \hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) \\ & + \hat{H}_{\text{rel}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0), \end{aligned} \quad (1)$$



**FIG. 1.** The scheme of interaction between helium atoms. Vector  $\mathbf{R}_0$  is displayed schematically as a part of  $z$ -axis, i.e., at  $\Theta_0 = 0$ .

where  $\mu = M_{\text{nuc}}/m_e$  ( $M_{\text{nuc}}$  is nuclear mass),  $H^{(e)}$  is the pure electronic part of the problem (four mutually repulsing electrons in the attractive Coulomb central fields of the both first and second nucleus),

$$\hat{H}^{(e)}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) = -\frac{1}{2} \sum_s \Delta^{(e)}(\mathbf{r}_s) - Z_0 \sum_s \frac{1}{r_s} \quad (2)$$

and

$$\hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = -Z_0 \sum_s \frac{1}{|\mathbf{r}_s - \mathbf{R}_0|} + \frac{1}{2} \sum_{s \neq s'} \frac{1}{r_{ss'}}, \quad (3)$$

where  $\mathbf{r}_{ss'} = \mathbf{r}_s - \mathbf{r}_{s'}$ ,  $s, s' = a, b, c, d$ . Furthermore,  $\hat{H}_{\text{rel}}$  describes the relativistic corrections due to spin-orbit (SO) and spin-spin (SS) interactions,<sup>10</sup>

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{SO}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) + \hat{H}_{\text{SS}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d). \quad (4)$$

The spin-orbit term has the form (cmp. with  $H_3$  in Eq. (39.14) of the Ref. 16)

$$\begin{aligned} \hat{H}_{\text{SO}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = & -i \frac{Z_0 g_S \alpha_S^2}{4} \left\{ \sum_s \hat{\sigma}_s \left[ \frac{\mathbf{r}_s}{r_s^3} \times \nabla_s \right] \right. \\ & + \sum_s \hat{\sigma}_s \left[ \frac{\mathbf{r}_s - \mathbf{R}_0}{|\mathbf{r}_s - \mathbf{R}_0|^3} \times \nabla_s \right] \\ & \left. - \frac{1}{Z_0} \sum_s \hat{\sigma}_s \sum_{s' \neq s} \left[ \frac{\mathbf{r}_{ss'}}{r_{ss'}^3} \times (\nabla_s - \nabla_{s'}) \right] \right\}, \end{aligned} \quad (5)$$

where  $\alpha_S = 1/137.039$  is Sommerfeld constant,  $g_S = 1.001145$  is spin  $g$ -factor, and  $\sigma$  is the vector with components built of Pauli matrices,

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Thomas-Frenkel factor  $1/2$  has been taken into account in Eq. (77) as well. The spin-spin interaction term describes the pair interaction between magnetic moments of individual electrons (cmp. with  $H_5$  in Eq. (39.14) of the Ref. 16),

$$\begin{aligned} \hat{H}_{\text{SS}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) = & \frac{g_S^2 \alpha_S^2}{4} \left\{ -\frac{8\pi}{3} \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'} \delta(\mathbf{r}_{ss'}) \right. \\ & \left. + \sum_{s \neq s'} \frac{1}{r_{ss'}^3} \left[ \hat{\sigma}_s \hat{\sigma}_{s'} - 3 \frac{(\mathbf{r}_{ss'} \cdot \hat{\sigma}_s)(\mathbf{r}_{ss'} \cdot \hat{\sigma}_{s'})}{r_{ss'}^2} \right] \right\} \end{aligned} \quad (6)$$

(nuclear spin of the  $^4\text{He}$  atom is equal to zero). It is quite evident that the spin-spin Hamiltonian  $\hat{H}_{\text{SS}}^{\hat{\sigma}}$  is explicitly independent on the internuclear distance  $\mathbf{R}_0$  (inexplicit dependence of spin-spin exchange is only due to  $R_0$ -dependent electronic matrix elements).<sup>10</sup>

It should be noted that the Hamiltonian Eq. (4) ignores so important relativistic corrections as retarded potentials for electromagnetic interactions within the intra- and interatomic bonds,<sup>16</sup>

but the proper treatment of the corresponding problem needs special relativistic approach based on Pauli equation with spinor basis. However, here we shall restrict our consideration to the non-relativistic problem of the helium-helium interatomic interactions, taken into account spin contribution only through parity and degeneration of the four-spin system on the helium-helium interatomic bond.

According to these suggestions the Hamiltonian Eq. (1) leads to the spinless Schrodinger equation,

$$\left\{ -\frac{1}{2\mu} \Delta^{(\text{nuc})}(\mathbf{R}_0) + \frac{Z_0^2}{R_0} + H^{(e)} + \hat{H}_{\text{int}} \right\} \times \Psi(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = \mathcal{E} \Psi(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0), \quad (7)$$

which describes an exact non-relativistic dynamics of the system, including internuclear motion, and spin contributions can be taken into account speculatively through parity and degeneration of the four-spin states on the interatomic helium-helium bond. In reality, when solving Eq. (7) within exact diagonalization approach, we have to take properly into account the dynamics of heavy repulsive nucleus and, thus, to use a basis incorporate the functions of continuous spectrum (with  $\mathcal{E} > 0$ ), whereas the electronic part of the problem is based only on functions of discrete spectrum.<sup>14</sup> However, if we are interested in some specific applications restricted to only interatomic interactions in condensed helium matter then the interatomic distance  $R_0$  has a rather narrow range of variation in the region of finite motion ( $\mathcal{E} < 0$ ), and the system can be treated on the semi-quantitative level within Heitler-London approximation,<sup>11</sup> where effective interatomic interaction  $U(R_0)$  is built as a parametric function of  $R_0$  with following treatment of  $R_0$  as dynamic variable in the one-dimensional  $R_0$ -dependent Schrodinger equation. Thus, below we will derive from Eq. (7) the density matrix  $\Psi(R_0)$  which depends only on the internuclear distance  $R_0$ . On the first step, in the next section we neglect the relativistic corrections  $H_{\text{rel}}$ , and discuss the corresponding corrections in Sec. 6.

### 3. COMPLETE SOLUTION

Thus, we present here solution of the complete non-relativistic Schrodinger equation Eq. (7) obtained within exact diagonalization approach. To do this, we choose the basis set for our problem as direct product,

$$u_p^{NLM}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | R_0, \Theta_0, \Phi_0) \equiv \begin{pmatrix} n_a & l_a & m_a \\ n_b & l_b & m_b \\ n_c & l_c & m_c \\ n_d & l_d & m_d \end{pmatrix} \otimes |NLM\rangle, \quad (8)$$

of electronic four-electron composition,

$$u_p(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) \equiv \begin{pmatrix} n_a & l_a & m_a \\ n_b & l_b & m_b \\ n_c & l_c & m_c \\ n_d & l_d & m_d \end{pmatrix} = \prod_s \psi_{n_s l_s m_s}(\alpha r_s, \vartheta_s, \varphi_s), \quad (9)$$

and nuclear wave function  $|NLM\rangle$ . Electronic wave function Eq. (9) is the vector composition which consists of hydrogen-like states

$$\Psi_{nlm}(\alpha \mathbf{r}) = \mathcal{R}_{nl}(\alpha r) Y_{lm}(\vartheta, \varphi) = |nlm\rangle, \quad (10)$$

and, consequently, the index  $p$  in Eq. (9) denotes a set of electronic single-particle indexes,

$$p \rightarrow \begin{pmatrix} n_a & l_a & m_a \\ n_b & l_b & m_b \\ n_c & l_c & m_c \\ n_d & l_d & m_d \end{pmatrix}, \quad (11)$$

where each of them is determined in univocal correspondence to a complete set of single-particle hydrogen-like quantum numbers. Further,  $Y_{lm}(\vartheta, \varphi)$  are spherical harmonics in standard determination,<sup>17,18</sup> and radial function  $\mathcal{R}_{nl}(\alpha r)$  depends on radial coordinate of an electron renormalized by scale parameter  $14] \alpha > 0$ . The radial function is

$$\mathcal{R}_{nl}(\alpha r) = -\frac{2\alpha^{3/2}}{n^2 \sqrt{\tau! \nu!}} \left( \frac{2\alpha r}{n} \right)^l \exp\left(-\frac{\alpha r}{n}\right) L_\tau^{(\lambda)}\left(\frac{2\alpha r}{n}\right), \quad (12)$$

where  $\tau = n - l - 1$ ,  $\lambda = 2l + 1$ ,  $\nu = n + l$ , and  $L_n^{(\lambda)}(x)$  are Laguerre polynomials<sup>19</sup>

$$L_\tau^{(\lambda)}(x) = \tau! (\lambda + \tau)! \sum_{k=0}^{\tau} \frac{(-x)^k}{k! (\tau - k)! (\lambda + k)!}. \quad (13)$$

With respect to Eq. (37) the radial functions  $\mathcal{R}_{nl}(\alpha r)$  can be represented in the explicit form,

$$\mathcal{R}_{nl}(\alpha r) = -\frac{2\alpha^{3/2}}{n^2} \sqrt{\tau! \nu!} \exp\left(-\frac{\alpha r}{n}\right) \sum_{k=0}^{\tau} \frac{(-1)^k \left(\frac{2\alpha r}{n}\right)^{k+l}}{k! (\tau - k)! (\lambda + k)!}. \quad (14)$$

The wave function for nuclear degrees of freedom is chosen in standard form,

$$\Psi_{NLM}(\mathbf{R}_0) = \mathcal{R}_{NL}(R_0) Y_{LM}(\Theta, \Phi) \equiv |NLM\rangle, \quad (15)$$

with the same radial function in Eq. (36) and Eq. (38). As a result, the corresponding matrix of the system has the form

$$\begin{aligned}
 H_{pq}^{N_1 N_2 L_1 L_2 M_1 M_2}(R_0) = & \left[ -\frac{Z_0^2}{2} \left( \frac{1}{n_a^2} + \frac{1}{n_b^2} + \frac{1}{n_c^2} + \frac{1}{n_d^2} + \frac{1}{\mu N_1^2} \right) \right] \delta_{pq} \delta_{N_1 N_2} \delta_{L_1 L_2} \delta_{M_1 M_2} + \left( Z_0^2 + \frac{Z_0}{\mu} \right) \left\langle N_1 \left| \frac{1}{R_0} \right| N_2 \right\rangle \delta_{pq} \delta_{L_1 L_2} \delta_{M_1 M_2} \\
 & + \frac{1}{2} \delta_{N_1 N_2} \delta_{L_1 L_2} \delta_{M_1 M_2} \sum_{s \neq s'} \left\langle \begin{matrix} n_{a_1} & l_{a_1} & m_{a_1} & n_{a_2} & l_{a_2} & m_{a_2} \\ n_{b_1} & l_{b_1} & m_{b_1} & n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_1} & l_{c_1} & m_{c_1} & n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_1} & l_{d_1} & m_{d_1} & n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \left| \frac{1}{|\mathbf{r}_s - \mathbf{r}_{s'}|} \right| \begin{matrix} n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \right\rangle \\
 & - Z_0 \sum_s \left\langle \begin{matrix} n_{a_1} & l_{a_1} & m_{a_1} & n_{a_2} & l_{a_2} & m_{a_2} \\ n_{b_1} & l_{b_1} & m_{b_1} & n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_1} & l_{c_1} & m_{c_1} & n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_1} & l_{d_1} & m_{d_1} & n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \left| \left\langle N_1 L_1 M_1 \left| \frac{1}{|\mathbf{r}_s - \mathbf{R}_0|} \right| N_2 L_2 M_2 \right\rangle \right| \begin{matrix} n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \right\rangle; (s, s' = a, b, c, d). \quad (16)
 \end{aligned}$$

The matrix elements from  $|\mathbf{r}_s - \mathbf{r}_{s'}|^{-1}$  (thus, correspondingly, from  $|\mathbf{r}_s - \mathbf{R}_0|^{-1}$ ) have been calculated analytically in Ref. 14. The algebraic representation Eq. (16) demonstrates explicitly the smallness of the contribution from kinetic energy of nuclear motion into the total energy of the system due to smallness of the coefficient  $\mu^{-1} \ll 1$ .

The matrix Eq. (16) has been diagonalized with basis Eq. (8) of 1134 functions (direct product of 81 electronic functions and 14 nuclear functions). The twenty five lowest levels of the obtained

spectrum are presented in Table I. Except the ground and the first excited states all the levels are degenerate, and each sub-level has a specific value of  $\langle R_0 \rangle$  which means a quantum fluctuation of inter-nuclear distance within a stable degenerated state. In other words, we have the “quantum oscillations” within the bound state of dimer. To prove the stability of the used diagonalization procedure we made the calculations with smaller basis of 405 elements. The results of the corresponding calculations are presented in Table II. It can be seen that such truncation of the basis has no effect on

**TABLE I.** Lowest levels of the complete  $^4\text{He}-^4\text{He}$  spectrum calculated with basis of 1134 elements.

Level	Energy, a.u.	State deg.	Nuclear quantum numbers, $\langle NLM \rangle$	$\langle R_0 \rangle$ , Bohr	$\langle R_0 \rangle$ , Å
1	-4.19415	1g	$\langle 210 \rangle$	3.229	1.708
2	-4.13701	1g	$\langle 100 \rangle$	4.382	2.318
3 <sub>1</sub>	-4.11761	2u	$\langle 21 \pm 1 \rangle$	3.243	1.715
3 <sub>2</sub>	-4.11761			3.401	1.799
4 <sub>1</sub>	-3.76090	3g	$\langle 200 \rangle$	3.464	1.885
4 <sub>2</sub>	-3.76090	3g		3.796	2.008
4 <sub>3</sub>	-3.76090	3g		3.826	2.024
5 <sub>1</sub>	-3.72043	3g	$\langle 210 \rangle$	3.209	1.698
5 <sub>2</sub>	-3.72043	3g		3.255	1.722
5 <sub>3</sub>	-3.72043	3g		3.315	1.753
6 <sub>1</sub>	-3.61646	6u	$\langle 21 \pm 1 \rangle$	3.074	1.626
6 <sub>2</sub>	-3.61646	6u		3.330	1.772
6 <sub>3</sub>	-3.61646	6u		3.422	1.810
6 <sub>4</sub>	-3.61646	6u		3.426	1.812
6 <sub>5</sub>	-3.61646	6u		3.492	1.847
6 <sub>6</sub>	-3.61646	6u		3.922	2.075
7 <sub>1</sub>	-3.59904	6u	$\langle 21 \pm 1 \rangle$	3.260	1.725
7 <sub>2</sub>	-3.59904	6u		3.271	1.731
7 <sub>3</sub>	-3.59904	6u		3.291	1.741
7 <sub>4</sub>	-3.59904	6u		3.305	1.749
7 <sub>5</sub>	-3.59904	6u		4.008	2.120
7 <sub>6</sub>	-3.59904	6u		4.010	2.121
8 <sub>1</sub>	-3.59493	3u	$\langle 210 \rangle$	3.458	1.829
8 <sub>2</sub>	-3.59493	3u		3.410	1.804
8 <sub>3</sub>	-3.59493	3u		3.411	1.805

**TABLE II.** Lowest levels of the complete  $^4\text{He}-^4\text{He}$  spectrum calculated with basis of 405 elements.

Level	Energy, a.u.	State deg.	Nuclear quantum numbers, $\langle NLM \rangle$	$\langle R_0 \rangle$ , Bohr	$\langle R_0 \rangle$ , Å
1	-4.1166	1g	$\langle 210 \rangle$	2.631	1.392
2	-4.0624	1g	$\langle 100 \rangle$	2.574	1.362
3 <sub>1</sub>	-4.0512	2u	$\langle 21 \pm 1 \rangle$	2.500	1.322
3 <sub>2</sub>	-4.0512			2.500	1.322
4 <sub>1</sub>	-3.6913	3g	$\langle 200 \rangle$	1.969	1.042
4 <sub>2</sub>	-3.6913	3g		1.951	1.032
4 <sub>3</sub>	-3.6913	3g		1.977	1.046
5 <sub>1</sub>	-3.6519	3g	$\langle 210 \rangle$	2.661	1.407
5 <sub>2</sub>	-3.6519	3g		2.553	1.350
5 <sub>3</sub>	-3.6519	3g		2.594	1.372
6 <sub>1</sub>	-3.5614	6u	$\langle 21 \pm 1 \rangle$	2.500	1.322
6 <sub>2</sub>	-3.5614	6u		2.500	1.322
6 <sub>3</sub>	-3.5614	6u		2.500	1.322
6 <sub>4</sub>	-3.5614	6u		2.500	1.322
6 <sub>5</sub>	-3.5614	6u		2.500	1.322
6 <sub>6</sub>	-3.5614	6u		2.500	1.322
7 <sub>1</sub>	-3.5411	6u	$\langle 21 \pm 1 \rangle$	2.500	1.322
7 <sub>2</sub>	-3.5411	6u		2.500	1.322
7 <sub>3</sub>	-3.5411	6u		2.500	1.322
7 <sub>4</sub>	-3.5411	6u		2.500	1.322
7 <sub>5</sub>	-3.5411	6u		2.500	1.322
7 <sub>6</sub>	-3.5411	6u		2.500	1.322
8 <sub>1</sub>	-3.5349	3u	$\langle 210 \rangle$	2.666	1.410
8 <sub>2</sub>	-3.5349	3u		2.668	1.411
8 <sub>3</sub>	-3.5349	3u		2.669	1.412

systematics of the obtained spectrum, and only absolute values of the level energies decrease approximately on less than 2%. It means that the Jacobi diagonalization provides an effective approach with correct reproduction of degenerate spectrum, and the real accuracy is restricted only by acceptable dimension of employed basis set (it is evident that the energies in the spectrum decrease very slowly as the basis becomes more and more wider and consequently increases the scope of calculations).

As is seen from Tables I and II the ground state (GS) of dimer is realized on non-spherical state  $|210\rangle$  of the nuclear subsystem, and, in view of screening of the nuclear field by electronic density from four electrons belong simultaneously for two nuclei [see Hamiltonian (1)], the total picture seems to be like as two interacting quadruples centered on the distance  $R_0$  (and the quadruples can be treated as superposition of the parallel and oppositely oriented dipoles from individual electrons formally belong to the separate nuclei). It is evident that there is no longer any compositions of the ground states of independent atoms, but superposition of elements built as direct composition [see Eq. (8)] of all elements belong to complete individual spectra of the interacting atoms.

It can be seen that the ground state energy of the system under study calculated even with the basis of 1134 elements ( $\sim -4.2$  a.u., within the basis of 405 elements this value is 2% higher) is nevertheless higher than the energy of two independent (non-interacting)  $^4\text{He}$  atoms in their ground states<sup>14</sup> ( $2 \times -2.86 = -5.72$  a.u.) which is consequence of the contribution to the total energy of  $^4\text{He}$ -dimer from mutual repulsion between oppositely oriented dipoles mutually inducted for each other by interacted atoms. The opposite orientation of the inducted dipolar momenta within the complete diatomic ground state is evident from the simple reasons of the spatial symmetry of the ground state wave function relative to the plane  $z = R_0/2$ . Attraction between two dipoles exists if the dipoles are parallel and lying along a common axis, but such configuration is in contradiction to the conditions of spatial symmetry for the ground state wave function. More detailed the problem of atom-atom interaction will be discussed below, in Sec. 4. In addition, as is shown by the Table I data, the average distance between nuclei is in good agreement with typical values of minima on potential curves known from literature.<sup>20–22</sup> But the most noticeable fact is that within degenerated states (the energies of sublevels have been calculated with high accuracy) the average internuclear distances  $\langle R_0 \rangle$  on the sublevels are evidently different, and this means existence of an “oscillatory state” of the corresponding degenerated level where the average internuclear distance  $\langle R_0 \rangle$  is “wandering” around the equivalent states of the degenerated level (degeneracy of the level is statistical weight of the degenerated state).

The obtained ground state ( $\sim -4.19$  a.u., see spectrum of Table I) has the “bound state energy” higher than the “vacuum level” of approximately  $-5.6$  a.u. (the energy of two independent helium atoms<sup>14</sup>), and in this connection the obtained result corresponds to a certain “metastable” state of the helium-helium bond and is due to following reasons. The total Hamiltonian of the problem Eq. (1) contains, in addition to the energy of two independent atoms [Eq. (2)], the internuclear repulsion and the interaction Hamiltonian (3) with pair interelectronic repulsion and attractions of each electron to the second nucleus proportional to the nuclear charge  $Z_0$ . Thus, the

corrections to the vacuum level are determined by the fine balance between attraction-repulsion within the many-body quantum system. In the strict sense, the corresponding problem cannot be solved rigorously only with the basis of discrete spectrum Eq. (8), but a basis of continuous spectrum must be included, and, in the common sense, the Green functions formalism should be applied. Such a scheme is beyond the scope of our consideration, and in the next section we analyze this problem from a certain semi-quantitative point of view to obtain some plausible estimations and clarify the corresponding facts on a qualitative level.

#### 4. LONG-RANGE INTERATOMIC INTERACTION

We start considering the problem from the simplest example of interaction between two hydrogen atoms (and below the used scheme will be easily generalized on the two-electron helium atoms with pair interactions between electrons) separated with internuclear distance  $R_0$ <sup>10</sup> (Fig. 2): two nuclei (denoted  $N_a, N_b$ ) with the positive charges  $Z_a = Z_b = Z_0 = +1$  (we use Hartree units) and coordinates  $\mathbf{R}_a = 0, \mathbf{R}_b = (0, 0, R_0) = \mathbf{R}_0$ , as well as two electrons ( $e_a, e_b$ ) with charges  $Z_a = Z_b = -1$  and coordinates  $\mathbf{r}_a, \mathbf{r}_b$ , centered (in order to make the best use the natural symmetry of the problem) on the corresponding nucleus, respectively. In view of  $\mu \gg 1$  we neglect below the kinetic energy of internuclear motion (so-called Born-Oppenheimer-Heitler-London approximation<sup>11</sup>) and rewrite the Hamiltonian (1) in the equivalent form<sup>10</sup> which, however, takes into account explicitly that the system consists of two initially independent spinless hydrogen atoms,

$$\hat{H}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = \hat{H}_a(\mathbf{r}_a) + \hat{H}_b(\mathbf{r}_b) + \hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0), \quad (17)$$

where

$$\hat{H}_a(\mathbf{r}_a) = -\frac{1}{2} \Delta^{(e_a)}(\mathbf{r}_a) - \frac{Z_0}{r_a}, \quad (18)$$

and

$$\hat{H}_b(\mathbf{r}_b) = -\frac{1}{2} \Delta^{(e_b)}(\mathbf{r}_b) - \frac{Z_0}{r_b}, \quad (19)$$

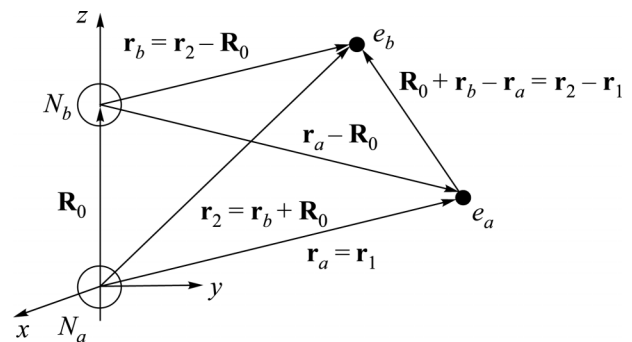


FIG. 2. The scheme of interaction between two spinless hydrogen atoms.

are Hamiltonians of non-perturbed hydrogen atoms (in addition,  $\mathbf{r}_1 = \mathbf{r}_a$  and  $\mathbf{r}_2 = \mathbf{r}_b - \mathbf{R}_0$ , see Fig. 2), and interatomic interaction energy is

$$\hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = + \frac{Z_0^2}{R_0} - \frac{Z_0}{|\mathbf{R}_0 - \mathbf{r}_a|} - \frac{Z_0}{|\mathbf{R}_0 + \mathbf{r}_b|} + \frac{Z_0}{|\mathbf{R}_0 + \mathbf{r}_b - \mathbf{r}_a|}. \quad (20)$$

Using Eqs. (18) and (19) we postulate that the electron  $a$  belongs to the nucleus  $N_a$ , and the electron  $b$  to  $N_b$ , respectively (Fig. 2), despite the electrons are principally undistinguished, as it is seen from Hamiltonian (1). Within the Born-Oppenheimer-Heitler-London approximation  $R_0$  is not the dynamical variable, but only a “free” parameter of the problem. Nevertheless, the applicability of the perturbation theory in the limit  $R_0 \rightarrow \infty$  needs a certain comment. The well-known multipolar expansion<sup>13,23</sup> of the interaction energy  $U(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_0)$  [Eq. (20)] is valid only under conditions

$$R_0 \gg r_a, \quad R_0 \gg r_b, \quad R_0 \gg |\mathbf{r}_b - \mathbf{r}_a|. \quad (21)$$

It means that within the standard approach we neglect the part of interatomic interaction which correspond to the case where one, or two, or all three inequalities in Eq. (21) might have an opposite sense. On the other hand, the conditions of Eq. (21) mean that the electron  $a$  attracts mainly to the nucleus  $N_a$ , the electron  $b$  attracts mainly to the nucleus  $N_b$ , and the rest of electrons-nuclei attraction is a correction to the interatomic interaction energy at  $R_0 \rightarrow \infty$ , and, in addition, the interelectron repulsion is the most essential at  $\mathbf{r}_a \rightarrow \mathbf{r}_b$ , which is, certainly, quite realistic. As a result, we conclude that the  $R_0^{-n}$ -expansion of  $U(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0)$  determined in accordance to Eq. (20) can give the qualitatively correct conclusion about the behavior of the interatomic interaction

$$U(\mathbf{R}_0) = \langle \Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b) | \hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) | \Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b) \rangle \quad (22)$$

averaged over the ground state  $\Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b)$  of the system of two one-electron hydrogen atoms.<sup>10</sup>

Expanding  $U(\mathbf{R}_0)$  up to quadruple-quadruple interaction  $\sim R_0^{-5}$ , we have

$$U(\mathbf{R}_0) = + \frac{Z_0^2}{R_0} - \frac{1}{R_0} + U_{dd} + U_{dQ} + U_{QQ} + \dots \quad (23)$$

where  $U_{dd} \sim R_0^{-3}$ ,  $U_{dQ} \sim R_0^{-4}$ ,  $U_{QQ} \sim R_0^{-5}$ , etc. The attractive first term  $1/R_0$  of Eq. (23) compensates exactly the internuclear repulsion of  $Z_0^2/R_0$  in Eq. (1) ( $Z_0 = +1$ ), so that the interatomic interaction at  $R_0 \rightarrow \infty$  does not contain the direct Coulomb terms and depends completely on the multipolar “tail” of Eq. (1). It can be shown easily that the similar result is also true for any pair of equivalent  $N$ -electron atoms (with nucleus charge  $NZ_0$ ) because internuclear repulsion  $Z_0^2/R_0$  is exactly compensated with attraction  $-NZ_0/R_0$  of  $N$  electrons possessed by one of the nuclei from another nucleus with  $Z_0 = N$ . In addition, the summary of terms with order  $\sim 1/R_0^2$  vanishes due to electroneutrality of the system. Thus, in the large distances  $R_0 \rightarrow \infty$  the multipolar expansion of

the  $U_{\text{int}}(R_0)$  begins from the master term of dipole-dipole interaction of order  $\sim 1/R_0^3$  (see also Refs. 13 and 23), and the term  $U_{dd}(R_0)$  in Eq. (23) is the dipole-dipole interaction averaged over the electronic degrees of freedom within the ground state of the diatomic complex,

$$U_{dd}(R_0) = D_{\alpha\beta}(\mathbf{R}_0) \langle \text{GS} | (x_a^\alpha x_b^\beta + x_b^\alpha x_a^\beta) | \text{GS} \rangle, \quad (24)$$

where greek indexes denote cartesian tensor components  $\alpha, \beta$ , etc.,  $\dots, = x, y, z$ , and

$$D_{\alpha\beta}(\mathbf{R}_0) = \frac{\delta_{\alpha\beta}}{R_0^3} - 3 \frac{R_0^\alpha R_0^\beta}{R_0^5}. \quad (25)$$

The second term,  $U_{dQ}(R_0)$ , is dipole-quadrupole interaction,

$$U_{dQ}(R_0) = D_{\alpha\beta\gamma}^{(q)}(\mathbf{R}_0) \langle \text{GS} | \{ x_a^\alpha x_b^\beta x_a^\gamma + x_a^\alpha x_b^\beta x_b^\gamma + x_b^\alpha x_a^\beta x_a^\gamma - x_b^\alpha x_b^\beta x_a^\gamma - x_b^\alpha x_a^\beta x_b^\gamma - x_a^\alpha x_b^\beta x_b^\gamma \} | \text{GS} \rangle, \quad (26)$$

where

$$D_{\alpha\beta\gamma}^{(q)}(\mathbf{R}_0) = \frac{3}{R_0^5} (\delta_{\alpha\beta} R_0^\gamma + \delta_{\alpha\gamma} R_0^\beta + \delta_{\beta\gamma} R_0^\alpha) - \frac{15}{R_0^7} R_0^\alpha R_0^\beta R_0^\gamma. \quad (27)$$

And the third term,  $U_{QQ}(R_0)$ , is quadrupole-quadrupole interaction,

$$U_{QQ}(R_0) = Q_{\alpha\beta\gamma\delta}(\mathbf{R}_0) \langle \text{GS} | \{ x_a^\alpha x_b^\beta x_a^\gamma x_b^\delta + x_a^\alpha x_b^\beta x_b^\gamma x_a^\delta + x_a^\alpha x_b^\beta x_a^\gamma x_a^\delta + x_b^\alpha x_a^\beta x_b^\gamma x_a^\delta + x_b^\alpha x_a^\beta x_a^\gamma x_b^\delta - x_a^\alpha x_b^\beta x_a^\gamma x_a^\delta - x_a^\alpha x_b^\beta x_b^\gamma x_a^\delta - x_a^\alpha x_b^\beta x_a^\gamma x_b^\delta - x_b^\alpha x_a^\beta x_b^\gamma x_a^\delta - x_b^\alpha x_a^\beta x_a^\gamma x_b^\delta - x_a^\alpha x_b^\beta x_b^\gamma x_b^\delta - x_b^\alpha x_a^\beta x_b^\gamma x_b^\delta - x_b^\alpha x_a^\beta x_a^\gamma x_b^\delta - x_b^\alpha x_b^\beta x_b^\gamma x_a^\delta \} | \text{GS} \rangle, \quad (28)$$

where

$$Q_{\alpha\beta\gamma\delta}(\mathbf{R}_0) = \frac{3}{R_0^5} (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\beta\gamma} \delta_{\alpha\delta}) - \frac{15}{R_0^7} (\delta_{\alpha\beta} R_0^\gamma R_0^\delta + \delta_{\alpha\gamma} R_0^\beta R_0^\delta + \delta_{\beta\gamma} R_0^\alpha R_0^\delta + \delta_{\alpha\delta} R_0^\beta R_0^\gamma + \delta_{\beta\delta} R_0^\alpha R_0^\gamma + \delta_{\gamma\delta} R_0^\alpha R_0^\beta) + \frac{105}{R_0^9} R_0^\alpha R_0^\beta R_0^\gamma R_0^\delta. \quad (29)$$

Note, that the accurate expansions like Eqs. (26)–(29) were proposed in due course by Van der Merwe.<sup>24,25</sup>

If  $R_0$  is oriented along  $z$ -axis as it shown on Fig. 2 then, after convolution over tensor indexes, Eqs. (24), (26) and (28) can be rewritten in more compact form,

$$U_{dd}(R_0) = \frac{2}{R_0^3} \langle \text{GS} | (x_a x_b + y_a y_b - 2z_a z_b) | \text{GS} \rangle, \quad (30)$$



(cmp. Flügge,<sup>18</sup> problem No. 161),

$$U_{dQ}(R_0) = \frac{9}{R_0^4} \langle GS | (x_a^2 + y_a^2)z_b + (x_b^2 + y_b^2)z_a + (x_a x_b + y_a y_b - 2z_a z_b)(z_a - z_b) | GS \rangle, \quad (31)$$

and

$$U_{QQ}(R_0) = \frac{18}{R_0^5} \langle GS | r_a^2 r_b^2 + 2(\mathbf{r}_a \mathbf{r}_b)^2 - 5[r_a^2 z_b^2 + r_b^2 z_a^2 + 3(\mathbf{r}_a \mathbf{r}_b)z_a z_b] + 35z_a^2 z_b^2 - 2\mathbf{r}_a \mathbf{r}_b(\mathbf{r}_a^2 + \mathbf{r}_b^2) + 10[(\mathbf{r}_a^2 + \mathbf{r}_b^2)z_a z_b + (\mathbf{r}_a \mathbf{r}_b)(z_a^2 + z_b^2)] - \frac{70}{3}(z_a^2 + z_b^2)z_a z_b | GS \rangle. \quad (32)$$

The next step is to find the average of the potential energy Eqs. (30)–(32) over ground state of the problem. If, as usual, the potential energy is considered as perturbation, then unperturbed Hamiltonian

$$\hat{H}_0(\mathbf{r}_a, \mathbf{r}_b) = \hat{H}_a(\mathbf{r}_a) + \hat{H}_b(\mathbf{r}_b)$$

[see Eqs. (73) and (74)] has the spectrum

$$E_{n_a n_b}^{(0)} = \frac{Z_0^2}{2} \left\{ \frac{1}{n_a^2} + \frac{1}{n_b^2} \right\}$$

with eigenfunctions

$$u_q(\mathbf{r}_a, \mathbf{r}_b) = \psi_{n_a l_a m_a}(\mathbf{r}_a) \otimes \psi_{n_b l_b m_b}(\mathbf{r}_b), \quad (33)$$

where index

$$q \rightarrow \left\{ \begin{matrix} n_a & l_a & m_a \\ n_b & l_b & m_b \end{matrix} \right\} \quad (34)$$

denotes the complete set of the quantum numbers of the unperturbed diatomic problem. Furthermore,

$$\psi_{nlm}(\alpha \mathbf{r}) = \mathcal{R}_{nl}(\alpha r) Y_{lm}(\vartheta, \varphi) \equiv |nlm\rangle, \quad (35)$$

are single-particle hydrogen-like functions,<sup>17,26</sup> where  $Y_{lm}(\vartheta, \varphi)$  are spherical harmonics in standard determination,<sup>17,27</sup> and radial function  $\mathcal{R}_{nl}(\alpha r)$  depends on radial coordinate renormalized by scale parameter<sup>14,18,28</sup>  $\alpha = Z_0 - \sigma > 0$  ( $\sigma$  is screening parameter,<sup>28–31</sup> below we put  $\alpha = Z_0$ ,  $\sigma = 0$ ), and the radial function is

$$\mathcal{R}_{nl}(\alpha r) = -\frac{2\alpha^{3/2}}{n^2 \sqrt{(n-l-1)! \sqrt{(n+l)!}}} \times \left( \frac{2\alpha r}{n} \right)^l \exp\left(-\frac{\alpha r}{n}\right) L_{n-l-1}^{(2l+1)}\left(\frac{2\alpha r}{n}\right), \quad (36)$$

where  $L_n^{(\lambda)}(x)$  are Laguerre polynomials,<sup>19</sup>

$$L_p^{(\lambda)}(x) = p!(\lambda + p)! \sum_{k=0}^p \frac{(-x)^k}{k!(p-k)!(\lambda + k)!}. \quad (37)$$

With respect to Eq. (37) the radial functions  $\mathcal{R}_{nl}(\alpha r)$  can be represented in the explicit form,

$$\mathcal{R}_{nl}(\alpha r) = -\frac{2\alpha^{3/2}}{n^2} \sqrt{\tau!} \sqrt{(n+l)!} \left( \frac{2\alpha r}{n} \right)^l \times \exp\left(-\frac{\alpha r}{n}\right) \sum_{k=0}^{\tau} \frac{(-1)^k}{k!} \frac{\left( \frac{2\alpha r}{n} \right)^k}{(\tau-k)!(2l+k+1)!}, \quad (38)$$

where  $\tau = n - l - 1$ . As an example of a proper use of the hydrogen basis for the many-electron problem we can refer to the paper.<sup>15</sup>

The ground state wave function corresponds to  $n_a = n_b = 1$  and  $l_a = l_b = m_a = m_b = 0$  and has the form

$$u_0(r_a, r_b) = \frac{1}{\pi} \exp\{-(r_a + r_b)\}, \quad E_{11}^{(0)} = Z_0^2 = 1. \quad (39)$$

The function Eq. (39) is not spherically symmetric because the vectors  $\mathbf{r}_a$  and  $\mathbf{r}_b$  have two-center orientation (see Fig. 2). After elementary integration we have  $U_{dd}(R_0) = 0$  and  $U_{dQ}(R_0) = 0$ , but

$$U_{QQ}(R_0) = -\frac{720}{R_0^5} < 0. \quad (40)$$

Thus, the quadruple-quadruple  $U_{QQ}(R_0)$  term calculated within well-known London's approach demonstrates nonzero attractive contribution  $\sim 1/R_0^5$  to the interatomic interaction energy just at the first order perturbation theory, instead of the presumed usually  $\sim 1/R_0^6$ -law expected for the dipole-dipole interaction through "second order perturbation theory". As a result, we conclude that the simple London's scheme (which is, in fact, a plain variational procedure), cannot give a well-determined answer about the asymptotic behavior of  $U_{\text{int}}(R_0)$  in the limit  $R_0 \rightarrow \infty$ . Below we discuss the corresponding problem from a more rigorous point of view.

## 5. INTERELECTRON REPULSION AS DISTURBANCE

For the first step, we separate the attraction and repulsion in the total interaction energy of the system. For this purpose we rewrite the complete Hamiltonian (1) in an equivalent form which is divided explicitly onto attractive ( $\hat{H}^{(\text{attr})}$ ) and repulsive ( $\hat{H}^{(\text{rep})}$ ) parts,

$$\hat{H}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = \hat{H}^{(\text{attr})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) + \hat{H}^{(\text{rep})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0), \quad (41)$$

where the attractive part,

$$\hat{H}^{(\text{attr})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = \hat{H}'_a(\mathbf{r}_a) + \hat{H}'_b(\mathbf{r}_b), \quad (42)$$

with

$$\hat{H}'_a(\mathbf{r}_a) = -\frac{1}{2} \Delta^{(e_a)}(\mathbf{r}_a) - \frac{Z_0}{r_a} - \frac{Z_0}{|\mathbf{R}_0 - \mathbf{r}_a|} \quad (43)$$

and

$$\hat{H}'_b(\mathbf{r}_b) = -\frac{1}{2} \Delta^{(e_b)}(\mathbf{r}_b) - \frac{Z_0}{r_b} - \frac{Z_0}{|\mathbf{R}_0 + \mathbf{r}_b|} \quad (44)$$

includes attraction of both electrons to the both (host and foreign) nuclei of the two-center problem, and, correspondingly, the repulsive part,

$$\hat{H}^{(\text{rep})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = + \frac{Z_0^2}{R_0} + \hat{V}^{(ee)}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0), \quad (45)$$

which consists of internuclear,  $Z_0^2/R_0$ , and interelectronic,

$$\hat{V}^{(ee)}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = + \frac{1}{|\mathbf{R}_0 - \mathbf{r}_a + \mathbf{r}_b|}, \quad (46)$$

Coulomb repulsions. It means, that the problem is presented as superposition of the Hamiltonian  $\hat{H}^{(\text{attr})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0)$  for the two independent, mutually non-interacting electrons which belong to the both attractive nuclei (this Hamiltonian will be considered below as “non-perturbed” part of the two-center problem) and repulsive part  $\hat{H}^{(\text{rep})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0)$  which is Coulomb interaction between two electrons and the similar repulsion between two immobile nuclei, respectively.

### 5.1. Attraction to the nuclei

The spectrum of non-perturbed part  $\hat{H}^{(\text{attr})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0)$  of the Hamiltonian can be built within an exact diagonalization procedure using basis Eq. (33), as it proposed in Refs. 10, 14, and 32 for helium atom and helium dimer. The corresponding matrix representation for this part has the form

$$\hat{H}_{pq}^{(\text{attr})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = - \frac{Z_0^2}{2} \left( \frac{1}{n_a^2} + \frac{1}{n_b^2} \right) \delta_{pq} + \hat{H}_{pq}^{(\text{for})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0), \quad (47)$$

where

$$\begin{aligned} \hat{H}_{pq}^{(\text{for})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = & - \left\langle n_a l_a m_a \left| \frac{Z_0}{|\mathbf{R}_0 - \mathbf{r}_a|} \right| n_a l_a m_a \right\rangle \delta_b \\ & - \left\langle n_b l_b m_b \left| \frac{Z_0}{|\mathbf{R}_0 - \mathbf{r}_b|} \right| n_b l_b m_b \right\rangle \delta_a, \end{aligned} \quad (48)$$

with

$$\delta_a = \delta_{n_a l_a m_a} \delta_{l_{a1} l_{a2}} \delta_{m_{a1} m_{a2}}, \quad \delta_b = \delta_{n_b l_b m_b} \delta_{l_{b1} l_{b2}} \delta_{m_{b1} m_{b2}}.$$

The first term in Eq. (47) is diagonal matrix element which describes the energy of two independent atoms. The term  $\hat{H}_{pq}^{(\text{for})}(\mathbf{R}_0)$  is attraction to the “foreign” nuclei, and the corresponding matrix elements can be calculated analytically as it was made recently in Refs. 10 and 32. As a result we have ( $\mathbf{R}_0$  is oriented along  $z$ -axis, see Fig. 2, and scaling coefficient<sup>14</sup>  $\alpha = Z_0$ )

$$\begin{aligned} & \left\langle n_1 l_1 m_1 \left| \frac{1}{|\mathbf{R}_0 - \mathbf{r}|} \right| n_2 l_2 m_2 \right\rangle \\ & = \sqrt{(2l_1 + 1)(2l_2 + 1)} \sum_{l=l_{\min}}^{l_{\max}} \mathcal{I}_l \left( \begin{matrix} n_1, & l_1 \\ n_2, & l_2 \end{matrix} \middle| \alpha R_0 \right) \Phi_l(l_1, m_1 | l_2, m_2), \end{aligned} \quad (49)$$

and

$$\begin{aligned} & \left\langle n_1 l_1 m_1 \left| \frac{1}{|\mathbf{R}_0 + \mathbf{r}|} \right| n_2 l_2 m_2 \right\rangle \\ & = \sqrt{(2l_1 + 1)(2l_2 + 1)} \sum_{l=l_{\min}}^{l_{\max}} (-1)^l \mathcal{I}_l \left( \begin{matrix} n_1, & l_1 \\ n_2, & l_2 \end{matrix} \middle| \alpha R_0 \right) \Phi_l(l_1, m_1 | l_2, m_2). \end{aligned} \quad (50)$$

Here

$$\Phi_l(l_1, m_1 | l_2, m_2) = \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \sum_{m=-l}^l (-1)^{m+m_1} \begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_2 & m \end{pmatrix}, \quad (51)$$

where  $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$  are  $3j$ -symbols,<sup>27</sup>  $l_{\min} = |l_1 - l_2|$ ,  $l_{\max} = l_1 + l_2$  and  $m_1 - m_2 = m$ . Furthermore,

$$\begin{aligned} \mathcal{I}_l \left( \begin{matrix} n_1, & l_1 \\ n_2, & l_2 \end{matrix} \middle| \alpha R_0 \right) = & \frac{4}{n_1^2 n_2^2} \frac{\sqrt{\tau_1! \tau_2! \nu_1! \nu_2!}}{a^{l_1+l_2+2}} \left( \frac{2}{n_1} \right)^{l_1} \left( \frac{2}{n_2} \right)^{l_2} \sum_{k_1=0}^{\tau_1} \sum_{k_2=0}^{\tau_2} \frac{(-1)^{k_1+k_2}}{a^{k_1+k_2} k_1! k_2!} \frac{\left( \frac{2}{n_1} \right)^{k_1} \left( \frac{2}{n_2} \right)^{k_2}}{(\lambda_1 + k_1)! (\lambda_2 + k_2)! (\tau_1 - k_1)! (\tau_2 - k_2)!} \\ & \times \left\{ \frac{(l + N + 2)!}{(a\alpha R_0)^{l+1}} \left[ 1 - \exp(-a\alpha R_0) \sum_{k=0}^{l+N+2} \frac{(a\alpha R_0)^k}{k!} \right] + (a\alpha R_0)^l (N - l + 1)! \exp(-a\alpha R_0) \sum_{k=0}^{N-l+1} \frac{(a\alpha R_0)^k}{k!} \right\}, \end{aligned} \quad (52)$$

where  $a = n_1^{-1} + n_2^{-1}$ ,  $\tau_1 = n_1 - l_1 - 1$ ,  $\tau_2 = n_2 - l_2 - 1$ ,  $\nu_1 = n_1 + l_1$ ,  $\nu_2 = n_2 + l_2$ ,  $\lambda_1 = 2l_1 + 1$ ,  $\lambda_2 = 2l_2 + 1$ , and  $N = l_1 + l_2 + k_1 + k_2$ , and  $\alpha = Z_0 = 1$ .

At  $R_0 \rightarrow \infty$  the integral Eq. (52) behaves like Laurent series expansion over  $(a\alpha R_0)^{-l}$ ,

$$\mathcal{I}_l \left( \begin{matrix} n_1, & l_1 \\ n_2, & l_2 \end{matrix} \middle| \alpha R_0 \rightarrow \infty \right) \sim \frac{(l + N + 2)!}{a^{N+2}} \frac{1}{(a\alpha R_0)^{l+1}}. \quad (53)$$

At  $R_0 \rightarrow 0$  has the finite limit



$$\mathcal{I}_l \left( \begin{matrix} n_1, & l_1 \\ n_2, & l_2 \end{matrix} \middle| \alpha R_0 = 0 \right) = \frac{(N+1)!}{a^{N+2}} \delta_{l,0}, \quad (54)$$

and Eq. (49) [as well as Eq. (50), correspondingly] transforms exactly into matrix element  $\langle n_1 l_1 m_1 | r^{-1} | n_2 l_2 m_2 \rangle$  [see Eqs. (28), (29) in Ref. 14].

The attractive part  $U^{(\text{attr})}(R_0)$  of the interatomic interaction energy can be obtained as the matrix element over the ground state of undisturbed attractive operator  $\hat{H}_{pq}^{(\text{attr})}(\mathbf{R}_0)$  [Eq. (47)],

$$U^{(\text{attr})}(R_0) = \langle \Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) | \hat{H}_{pq}^{(\text{attr})}(\mathbf{R}_0) | \Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) \rangle, \quad (55)$$

where the ground state wave function  $\Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0)$  found through exact diagonalization procedure on the matrix  $\hat{H}_{pq}^{(\text{attr})}(\mathbf{R}_0)$  has the form

$$\begin{aligned} \Psi^{(\text{GS})} = & a_{11}(R_0) |100\rangle_a |100\rangle_b + a_{12}(R_0) (|100\rangle_a |200\rangle_b \\ & + |200\rangle_a |100\rangle_b) + a_{22}(R_0) |200\rangle_a |200\rangle_b \\ & + \sum_{n_a, n_b=3}^{\infty} a_{n_a n_b}(R_0) |n_a 00\rangle_a |n_b 00\rangle_b, \end{aligned} \quad (56)$$

where  $a_{21} = a_{12}$ . In the case of the used here basis  $N_{\text{bas}} = 25$  ( $n_a, n_b \leq 2$ ) the explicit expression for this function is

$$\begin{aligned} \Psi^{(\text{GS})}(\mathbf{r}_a, \mathbf{r}_b | \mathbf{R}_0) = & \frac{1}{\pi} \left\{ a_{11}(R_0) \exp[-(r_a + r_b)] \right. \\ & + \frac{a_{12}(R_0)}{2\sqrt{2}} \left\langle \left( 1 - \frac{r_b}{2} \right) \exp \left[ -\left( r_a + \frac{r_b}{2} \right) \right] \right. \\ & + \left. \left( 1 - \frac{r_a}{2} \right) \exp \left[ -\left( r_b + \frac{r_a}{2} \right) \right] \right\rangle \\ & + \frac{a_{22}(R_0)}{8} \left( 1 - \frac{r_a}{2} \right) \left( 1 - \frac{r_b}{2} \right) \exp \left[ -\frac{1}{2}(r_a + r_b) \right] \Big\} \\ & + \sum_{n_a, n_b=3}^{25} a_{n_a n_b}(R_0) |n_a 00\rangle_a |n_b 00\rangle_b. \end{aligned} \quad (57)$$

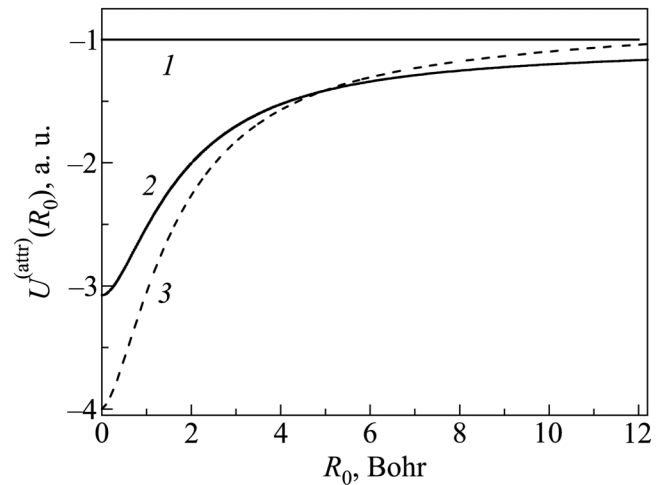
The coefficients  $a_{11}$ ,  $a_{12} = a_{21}$ , and  $a_{22}$  for the ground state wave function Eq. (57) obtained with the basis of  $N_{\text{bas}} = 25$  are presented in Table III as functions of internuclear distance  $R_0$  (the contribution from the last sum in Eq. (56) is less than 3% at  $R_0 \sim 1$  and becomes negligible small at  $R_0 \gg 1$ ). It can be seen that the main weight in the ground state composition (especially at large distances) has the basis component  $|100\rangle_a |100\rangle_b$  which makes the used basis quite similar (with accuracy of a few percents) to the simple basis Eq. (33).

The average  $U^{(\text{attr})}(R_0)$  of the operator Eq. (42) as the function of internuclear distance  $R_0$  is plotted on the Fig. 3. The upper line 1 is the energy of two independent electrons  $U^{(\text{attr})}(R_0) = -1.0$  [the first term in Eq. (47)] attracting to the nuclei with  $Z_0 = 1$ , namely, the energy of two independent hydrogen atoms in the ground states on infinite large distance. Account of the attraction

**TABLE III.** Coefficients  $a_{ij}$  ( $R_0$ ) in the ground state wave function of  $N_{\text{bas}} = 25$  [Eq. (57)].

$R_0$ , Bohr	$a_{11}$	$a_{12} = a_{21}$	$a_{22}$
0.00	0.9685535	0.1745211	0.0314465
1.00	0.9663071	0.1202303	0.0149593
2.00	0.9566278	0.0385858	0.0015564
3.00	0.9549562	-0.0177861	0.0003313
4.00	0.9650734	-0.0387711	0.0015576
5.00	0.9789732	-0.0359337	0.0013190
6.00	0.9887988	-0.0257436	0.0006702
7.00	0.9940432	-0.0168412	0.0002853
8.00	0.9966541	-0.0108371	0.0001178
9.00	0.9979926	-0.0070754	0.0000502
10.00	0.9987220	-0.0047397	0.0000225
11.00	0.9991455	-0.0032664	0.0000107
12.00	0.9994055	-0.0023138	0.0000054

to the foreign nuclei makes the energy  $U^{(\text{attr})}(R_0)$  the lower the smaller is the distance  $R_0$ , and in the limit  $R_0 = 0$  we should expect  $U^{(\text{attr})}(0) = -4.0$  (two independent electrons in the central Coulomb field with  $Z_0 = 2$ ). However, to get this limit within diagonalization procedure we need use undoubtedly the basis of infinity dimension. Indeed, despite in the limit  $R_0 \rightarrow 0$  the contribution into sums of Eqs. (49) and (50) give only elements with  $l_1 = l_2$ , there are infinite set of elements satisfying to this case at simultaneous condition  $n_1 \neq n_2$ . The practical calculations show that the limiting value  $U^{(\text{attr})}(0)$  very slow tends to the 4.0 with  $N_{\text{bas}} \rightarrow \infty$  the curve 2 on Fig. 3 shows the result for the basis of  $N_{\text{bas}} = 25$  elements ( $n_1, n_2 \leq 2$ ) with the limit  $U^{(\text{attr})}(0) = -3.0755$ . The calculations with



**FIG. 3.** Attraction part  $U^{(\text{attr})}(R_0)$  of the total energy  $U(R_0)$  of the  $\text{H}_2$ -complex [spectrum of the matrix Eq. (42) as function of  $R_0$ ]: energy of attraction of two independent electrons to the nuclei with  $Z_0 = 1$  (two isolated hydrogen atoms in the ground state) (1); spectrum calculated with the basis Eq. (35) of  $N_{\text{bas}} = 25$  elements ( $U^{(\text{attr})}(0) = -3.0755$ ) (2); the Padé extrapolated spectrum  $U^{(\text{attr})}_{(\text{ext})}(R_0)$  of the attractive part in the limit  $N_{\text{bas}} \rightarrow \infty$  ( $U^{(\text{attr})}(0) = -4.0$ ) (3).

basis of  $N_{\text{bas}} = 3025$  elements ( $n_1, n_2 \leq 5$ ) demonstrate the limit only  $U^{(\text{attr})}(0) = -3.10890$  and, hence, this curve practically coincides with the dependence obtained for  $N_{\text{bas}} = 25$ . Thus, there is no reason to plot the set of curves with different  $N_{\text{bas}}$ , except of limiting dependence of  $N_{\text{bas}} \rightarrow \infty$ . This dependence can be obtained through extrapolation which can be built through replacement of the operator  $\hat{H}_{pq}^{(\text{for})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0)$  in Eq. (47) with the renormalized operator

$$\hat{H}_{pq}^{(\text{for})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) \rightarrow \kappa(R_0, N_{\text{bas}})\hat{H}_{pq}^{(\text{for})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0). \quad (58)$$

The function  $\kappa(R_0, N_{\text{bas}})$  for our calculations with  $N_{\text{bas}} = 25$  is chosen as

$$\kappa(R_0, 25) = 1.0 + 0.43992623 \exp(-0.2R_0). \quad (59)$$

In addition, we note that the curve 2 on Fig. 3 is not so proper tending to the limit  $U^{(\text{attr})}(\infty) = -1$ . In this connection we correct the dependence  $U^{(\text{attr})}(R_0)$  with coefficient  $\exp(-0.01R_0)$ , so that the extrapolated attraction energy  $U_{(\text{ext})}^{(\text{attr})}(R_0)$  has the form

$$U_{(\text{ext})}^{(\text{attr})}(R_0) = \langle \Psi^{(\text{GS})} | \hat{H}_{pq}^{(\text{for})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) | \Psi^{(\text{GS})} \rangle \exp(-0.01R_0). \quad (60)$$

This dependence has been presented on Fig. 3 (curve 3). In fact, the expression (60) is a modified Padé approximation for attractive energy of the system under study.

The higher accuracy we expect to achieve in our calculations, the wider basis we must use for desirable goal. However, to build the physically adequate picture without enormous numerical calculations we restrict our consideration by described above basis with  $N_{\text{bas}} = 25$ , and the extrapolated function  $U_{(\text{ext})}^{(\text{attr})}(R_0)$  is used in all considerations below.

## 5.2. Interelectron repulsion

The repulsive part  $U^{(\text{rep})}(R_0)$  of the interaction energy is the average of the corresponding Hamiltonian  $\hat{H}^{(\text{rep})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0)$  Eq. (45) over the ground state Eqs. (56) and (57),

$$U^{(\text{rep})}(\mathbf{R}_0) = \langle \text{GS} | \hat{H}^{(\text{rep})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) | \text{GS} \rangle = \left\langle \text{GS} \left| \frac{Z_0^2}{R_0} \right| \text{GS} \right\rangle + U^{(\text{ee})}(\mathbf{R}_0), \quad (61)$$

where

$$U^{(\text{rep})}(\mathbf{R}_0) = \left\langle \text{GS} \left| \hat{V}^{(\text{ee})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) \right| \text{GS} \right\rangle. \quad (62)$$

The most complicated part of the problem under study is the electron-electron repulsion  $\hat{V}^{(\text{ee})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0)$  [Eq. (46)] within two-center geometry. The standard approach means that at  $R_0 \rightarrow \infty$  we have to present the average  $\langle \text{GS} | \hat{V}^{(\text{ee})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) | \text{GS} \rangle$  as expansion over  $1/R_0$ ,

$$U^{(\text{ee})}(\mathbf{R}_0) = \langle \text{GS} | \hat{V}^{(\text{ee})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) | \text{GS} \rangle = \sum_{n=1}^{\infty} \frac{a_n(R_0)}{R_0^n}, \quad (63)$$

where, in general, the coefficients  $a_n(R_0)$ , calculated as averages on the basis Eq. (56) must be undoubtedly  $R_0$ -dependent. In this sense the expansion (63) is not pure power-like, nevertheless, we will classify the terms of this expansion by the powers of  $1/R_0^n$ .

The main problem of the representation Eq. (63) is that the manifold of irregularities for the operator Eq. (46) (it is the simple Coulomb manifold  $|\mathbf{R}_0 - \mathbf{r}_a + \mathbf{r}_b| = 0$ ) has been mapped into the unique essentially irregular point  $R_0 = \infty$ , which principally destructs and modifies the map of irregularities belong to the original Schrodinger equation [operator Eq. (41)]. In this connection, the expression (63) can be considered as an estimation which gives a result of a qualitative level, and, for definiteness sake, we have to discuss the case  $R_0 \rightarrow 0$  as well,

$$U^{(\text{ee})}(\mathbf{R}_0) = \left\langle \text{GS} \left| \hat{V}^{(\text{ee})}(\mathbf{r}_a, \mathbf{r}_b|\mathbf{R}_0) \right| \text{GS} \right\rangle = \sum_{n=0}^{\infty} b_n(R_0) R_0^n. \quad (64)$$

Both expressions Eq. (63) and Eq. (64) must be sewn together in an intrinsic point of the interval  $0 \leq R_0 < \infty$ . It is evident that  $R_S$  as the boundary point between  $\sim R_0^n$  and  $\sim 1/R_0^n$  expansions is the value of order unity,  $R_S \sim 1$ .

To make the corresponding estimations, we use the expansions  $(\mathbf{r}_{ab} = \mathbf{r}_a - \mathbf{r}_b \equiv \mathbf{r}_{ab}^a)$ ,

$$\frac{1}{|\mathbf{R}_0 - \mathbf{r}_{ab}|} \simeq \frac{1}{r_{ab}} + \frac{\mathbf{r}_{ab} \mathbf{R}_0}{r_{ab}^3} - \frac{\delta_{ab} R_0^2}{r_{ab}^3} + 3 \frac{r_{ab}^\alpha r_{ab}^\beta R_0^\alpha R_0^\beta}{r_{ab}^5} + \dots \quad (65)$$

at  $R_0 \ll r_{ab}$  (in practical situation at  $R_0 < 1$ ). The average of the first term in Eq. (65) is similar to direct interaction  $|\mathbf{r}_a - \mathbf{r}_b|^{-1}$  of two electrons within a unitary coordinate system (see Ref. 14), it has integrable irregularity which was discussed in the context of the interelectron repulsion in the helium atom.<sup>10,14</sup> The average of the second term (proportional to  $R_0$ ) in Eq. (65) is equal to zero because this term is odd function of  $\mathbf{r}_a - \mathbf{r}_b$  relative to the two-electron permutation (the interaction energy must be invariant relative to the pair electron permutation  $a \rightarrow b$ ). The averages of the terms  $1/r_{ab}^3$  and  $1/r_{ab}^5$  contain the logarithmic divergencies usually prepared within the framework of quantum electrodynamics procedure.<sup>33</sup> Divergencies of such kind appear during calculation of the relativistic spin-orbital and spin-spin corrections for the matrix elements of the problem, but this question is beyond the purpose of our consideration. Divergencies of the higher terms are non-physical, and must be ignored. Thus, in general, for the case  $R_0 \leq 1$  we obtain the  $U^{(\text{ee})}(\mathbf{R}_0)$  as divergent asymptotic series, and within the common procedure of asymptotical representations<sup>34</sup> we have to restrict ourselves by the regular part of asymptote. So, for the case  $R_0 \leq 1$  we have to use asymptotics

$$U^{(\text{rep})}(\mathbf{R}_0) = \frac{1}{R_0} + \left\langle \text{GS} \left| \frac{1}{|\mathbf{r}_a - \mathbf{r}_b|} \right| \text{GS} \right\rangle. \quad (66)$$

Figure 4 presents the average energy of the system (with repulsive energy  $U^{(\text{rep})}(R_0)$  calculated in the limit  $R_0 < 1$ ) as a function of the internuclear distance  $R_0$ . It is seen that the dependence  $U(R_0)$  demonstrates rather narrow region (red line between points A and B) where the total energy of the system is lower than the

ground state of two independent atoms and, consequently, a bound state of the atoms can be realized. The depth of the potential well (relative to the “ground” level  $U(R_0) = -1$ ) is  $U(R_{\min}) = 0.495$  a.u.  $\simeq 12.5$  eV at the distance  $R_{\min} = 1.052$  Bohr  $= 0.557$  Å. These values are in good agreement with corresponding parameters known for hydrogen molecule.<sup>35</sup> The region right-hand of the

point B on the Fig. 4 corresponds to the dissociated states of H–H complex, i.e., mono-atomic form of hydrogen with repulsion between individual atoms experimentally observed in the Universe at very low density of the matter.<sup>36–40</sup>

At the opposite case,  $R_0 \gg r_{ab}$  the interelectron repulsion can be expanded formally over  $1/R_0^n$ ,

$$\begin{aligned} \frac{1}{|\mathbf{R}_0 - \mathbf{r}_{ab}|} &\simeq \frac{1}{R_0} + \frac{\mathbf{r}_{ab} \cdot \mathbf{R}_0}{R_0^3} - \frac{\delta_{\alpha\beta} x_{ab}^\alpha x_{ab}^\beta}{R_0^3} + 3 \frac{x_{ab}^\alpha x_{ab}^\alpha R_0^\beta}{R_0^5} + \left[ \frac{3}{R_0^5} (\delta_{\alpha\beta} R_0^\gamma + \delta_{\alpha\gamma} R_0^\beta + \delta_{\beta\gamma} R_0^\alpha) - \frac{15}{R_0^7} R_0^\alpha R_0^\beta R_0^\gamma \right] x_{ab}^\alpha x_{ab}^\beta x_{ab}^\gamma \\ &+ \left\{ \frac{3}{R_0^5} (\delta_{\alpha\beta} \delta_{\gamma\gamma} + \delta_{\alpha\gamma} \delta_{\beta\gamma} + \delta_{\beta\gamma} \delta_{\alpha\gamma}) - \frac{15}{R_0^7} (\delta_{\alpha\beta} R_0^\gamma R_0^\gamma + \delta_{\alpha\gamma} R_0^\beta R_0^\gamma + \delta_{\beta\gamma} R_0^\alpha R_0^\gamma + \delta_{\alpha\gamma} R_0^\beta R_0^\gamma + \delta_{\beta\gamma} R_0^\alpha R_0^\gamma + \delta_{\gamma\gamma} R_0^\alpha R_0^\beta) + \frac{105}{R_0^9} R_0^\alpha R_0^\beta R_0^\gamma R_0^\gamma \right\} x_{ab}^\alpha x_{ab}^\beta x_{ab}^\gamma x_{ab}^\gamma. \end{aligned} \quad (67)$$

The expression (65) is expended up to quadrupole-quadrupole interaction, similar to Eq. (28). Taking into account that  $R_0 = R_0(0,0,1)$ , we present the  $U^{(\text{rep})}(R_0)$  in the form quite similar to Eq. (23)

$$U^{(\text{rep})}(R_0) = \frac{Z_0^2}{R_0} + \frac{1}{R_0} + U_{dd}^{(\text{rep})} + U_{QQ}^{(\text{rep})} + \dots, \quad (68)$$

where

$$U_{dd}^{(\text{rep})}(R_0) = \frac{1}{R_0^3} \langle \text{GS} | 3z_{ab}^2 - r_{ab}^2 | \text{GS} \rangle \quad (69)$$

and

$$U_{QQ}^{(\text{rep})}(R_0) = \frac{3}{R_0^5} \langle \text{GS} | 3r_{ab}^4 - 30r_{ab}^2 z_{ab}^2 + 35z_{ab}^4 | \text{GS} \rangle \quad (70)$$

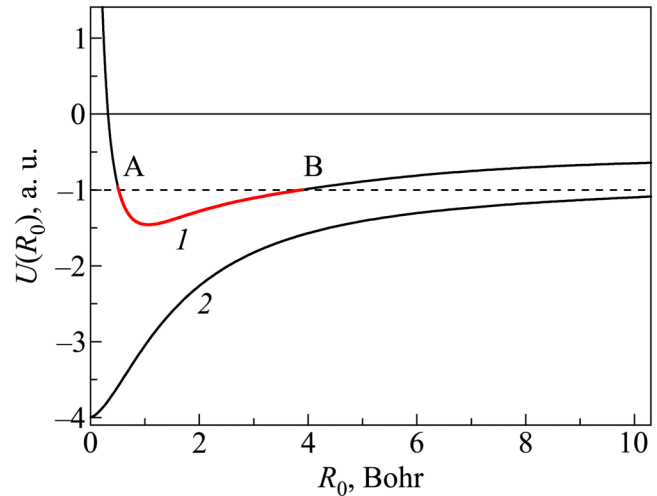
(the terms of  $1/R_0^2$  and  $1/R_0^4$  are equal to zero due to noninvariance to the pair electron permutation  $a \rightarrow b$ ). Recall, that  $U^{(\text{rep})}(R_0)$  Eq. (68) differs from the total interaction energy Eq. (23) by the attraction  $-2/R_0$  of the electrons to the nuclei (now this energy is included to  $U^{(\text{attr})}(R_0)$ , see curve 3 on the Fig. 3 and curve 2 on the Fig. 4).

Figure 5 presents three terms of Eq. (68). It can be seen that the magnitude of the quadrupole-quadrupole repulsion  $U_{QQ}^{(\text{rep})}(R_0)$  [Eq. (70)] is greater than dipole-dipole  $U_{dd}^{(\text{rep})}(R_0)$ , so that the expansion Eq. (68) at  $R_0 \rightarrow 0$  is divergent asymptotic series, just as the expansion Eqs. (65) and (66) at  $R_0 \rightarrow \infty$ . As it was mentioned above, this result is direct consequence of disregard for real integrable irregularity of two-point Coulomb potential interactions  $|\mathbf{R}_0 - \mathbf{r}_a + \mathbf{r}_b|^{-1}$  and replacement it by essentially singular point at  $R_0 = 0$  or non-physical irregularities in the terms of  $|\mathbf{r}_a - \mathbf{r}_b|^{-n}$ ,  $n > 3$ . The best way for an approximate description of the interelectron repulsion seems to be the direct calculations of the matrix elements for the Coulomb repulsion Eq. (66) in one-center coordinates.<sup>10,14,32</sup> However, to get the result with acceptable accuracy at large  $R_0$  we have to use a sufficiently large basis set. Moreover, to get an exact behavior of the system under study in the

limit  $R_0 \rightarrow \infty$  it need be probably taken into account not only states of discrete, but also continuous spectrum, as it known from the theory of atomic collisions.<sup>41</sup> In this connection our consideration is a semi-quantitative treatment which, nevertheless, gives correct physical picture of the problem under study. Figure 6 presents the total interatomic interaction energy  $U^{(\text{tot})}(\mathbf{R}_0)$ ,

$$\begin{aligned} U^{(\text{rep})}(\mathbf{R}_0) &= \langle \text{GS} | \hat{H}(\mathbf{r}_a, \mathbf{r}_b) | \text{GS} \rangle \\ &= U^{(\text{attr})}(R_0) + U^{(\text{rep})}(R_0), \end{aligned} \quad (71)$$

calculated with repulsion  $U^{(\text{rep})}(R_0)$  for small [Eq. (66), curve 1 on Fig. 6] and large [Eq. (68), curve 2 on Fig. 6] distances  $R_0$ . The



**FIG. 4.** (1) The total energy of the system  $U(R_0)$  with repulsive energy  $U^{(\text{rep})}(R_0)$  calculated in the limit  $R_0 < 1$ . The dashed line  $U(R_0) = -1$  is the energy of two independent hydrogen atoms in the ground state. The red part of the curve 1 between points A and B is the region of the bound state of the system. (2) The extrapolated attractive part of the  $U(R_0)$  (the same as the curve 3 on the plot Fig. 3).

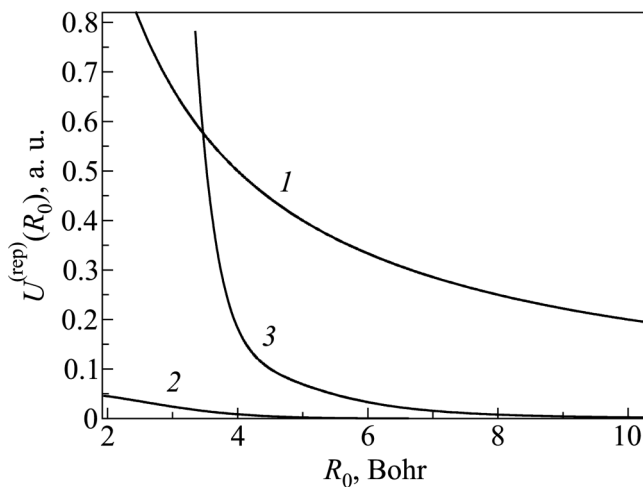


FIG. 5. The terms of Eq. (68):  $+2/R_0$  (1),  $U_{dd}^{(rep)}(R_0)$  (2), and  $U_{QQ}^{(rep)}(R_0)$  (3).

mentioned dependences intersect each other in the point C on Fig. 6, and it is reasonable to consider the vicinity of this point as a border of validity for the both asymptotics which can be matched continuously (by a certain interpolation procedure) within the intermediate border region to obtain the total dependence  $U(R_0)$  on half-axis  $0 < R_0 < \infty$ . The result is shown on Fig. 7.

The potential curve on Fig. 7(a) demonstrates two minima: the global minimum  $U_{gm} = -1.423$  a.u. at  $R_{gm} = 1.05$  Bohr belongs to the potential well which create the bound state  $U_0 \approx -1.162$  a.u. or  $-0.1645$  eV (relative to vacuum energy  $U = -1$  a.u.) at the average internuclear distance  $\langle R_0 \rangle = 1.4$  Bohr  $\approx 0.74$  Å

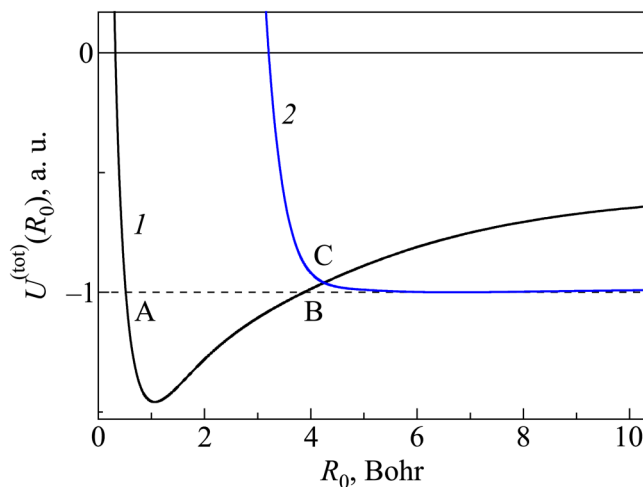


FIG. 6. The total interaction energy calculated with short-range repulsion asymptotics Eq. (66) (1); the total interaction energy calculated with long-range repulsion asymptotics Eq. (68) (2).

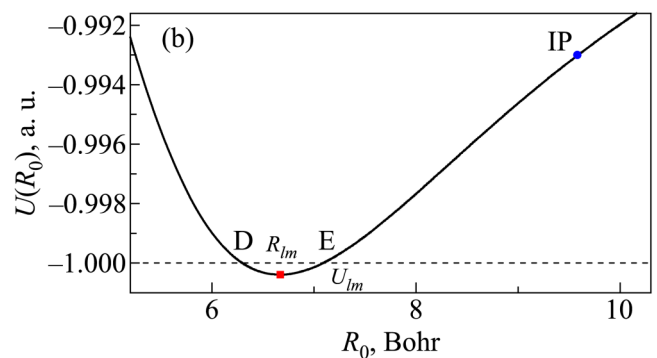
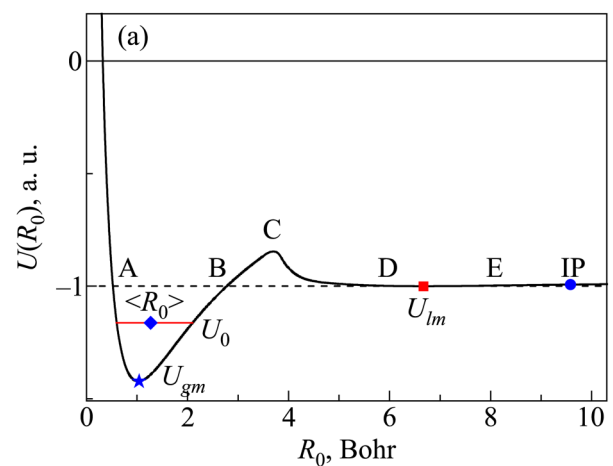


FIG. 7. (a) The total dependence of the interaction energy  $U(R_0)$  between two hydrogen atoms on the half-axis  $0 < R_0 < \infty$ . (b) The dependence  $U(R_0)$  in the vicinity of the local minimum  $U_{lm} = -1.00039$  a.u. at  $R_{lm} = 6.67$  Bohr  $\approx 3.53$  Å. The depth of the local minimum is not enough to create a bound state. The global minimum  $U_{gm} = -1.423$  a.u. at  $R_{gm} = 1.05$  Bohr belongs to the potential well which create the bound state  $U_0 \approx -1.162$  a.u. or  $-0.1645$  eV (relative to vacuum energy  $U = -1$  a.u.) at the average internuclear distance  $\langle R \rangle = 1.4$  Bohr  $\approx 0.74$  Å which evidently correspond to the known dissociation energy and the length of the interatomic bond for H<sub>2</sub> molecule<sup>35</sup> (see text).

which evidently correspond to the known dissociation energy and the length of the interatomic bond for H<sub>2</sub> molecule.<sup>35</sup> Certainly, this estimation is quite approximate because it based only on the primitive ground state averaging which does not take into account possibly intersections of the ground state with closely spaced excitation levels<sup>10</sup> and consequent various pre-dissociation effects.<sup>26</sup> On the right of the global minimum we have the potential barrier (the BCD region) which can produce some metastable states caused by tunneling through the BCD interval. The height of the barrier relative to the vacuum level  $U = -1$  is  $U_C = +0.154$  a.u.  $\approx 4.2$  eV at  $R_0 = 3.7$  Bohr.

The depth of the local minimum between points D and E on Fig. 7(b) ( $U_{lm} = -1.00039$  a.u. at  $R_{lm} = 6.67$  Bohr  $\approx 3.53$  Å) is not enough to create a bound state in this potential well. For corresponding estimation we note that the ground state in an ideal

parabolic potential well is  $\omega_0 = \sqrt{\partial^2 U(R_0)/\partial R_0^2}$  at  $R_0 = R_{lm}$ . In our case it gives an upper estimate with respect to the minimum of the potential well as  $\omega_0 = 5.66 \cdot 10^{-2}$  a.u., which is much higher than the level  $\omega_{IP} \simeq 7.4 \cdot 10^{-3}$  a.u. of the inflection point (IP) on the real non-parabolic potential [point IP on Fig. 7(b)]. Thus, the non-parabolic (nonharmonic) well near the  $U_{lm}$  is unable to confine any zero-point oscillation state.

As a result, the stable bound states of two hydrogen atoms ( $H_2$  molecule) are possible only inside of the interval AB, and within the interval BC they are metastable. On the right of the barrier the hydrogen atoms are moving separately, interacting through mutual repulsion. Of course, the obtained dependence  $U(R_0)$  on the left of the point B [Fig. 7(a)] can be considered only as a plain semi-quantitative description because the corresponding function is built as superposition of the formally exact (but calculated within truncated basis) attractive part and repulsive part which is formally divergent asymptotic series. In addition, we have to note that at  $R_0 \rightarrow \infty$  become essential corrections caused by long-range retarded interactions<sup>42</sup> (see also Refs. 16 and 23).

## 6. HE-HE INTERACTION

The most interesting topic in view of the problems discussed above is the interatomic interaction in helium which is commonly supposed to be an extremely quantum system (by the way, the hydrogen demonstrate a series of really quantum features that are no less important than well-known helium effects<sup>43</sup>). The main question is the root of the quantum nature of helium.

The real quantum nature of helium is the role of its spin subsystem in the helium-helium interatomic interaction. This role becomes quite evident when compare the quite different observable properties of two helium isotopes,  $^3\text{He}$  and  $^4\text{He}$ . Despite the only one-half nuclear spin of  $^3\text{He}$  (spin of  $^4\text{He}$  nucleus is equal to zero), it behaves radically different as compared to  $^4\text{He}$ . The main characteristic feature of  $^4\text{He}$  is  $\lambda$ -transition from simple liquid (He I) to so-called “superfluid” (He II) phase at 2.171 K under saturated vapor pressure.<sup>44</sup> It is clear that two simple liquids cannot be neighbored along the  $\lambda$ -line of the second order phase transition, so that, according to general physical reasons, the He II phase should be provided by a nonzero specific structural order parameter which can be realized only through the physical degrees of freedoms of the corresponding matter. The only difference between  $^3\text{He}$  and  $^4\text{He}$  (except of insufficient difference in atomic masses) is nuclear spin of  $^3\text{He}$ . Each phase transition observed in condensed matter is resulted inevitably by some details of interatomic interactions in this matter, and in the case of helium we have to conclude that the  $\lambda$ -transition is an effect of the spin subsystem of the helium isotopes. L. Shubnikov<sup>45</sup> was the first who pointed out the fact that the  $\lambda$ -transition seems to be a close analog of magnetic Curie transformation and proposed to interpret the He II phase as a liquid crystal, so that as the system with structural ordering (the Shubnikov’s proposition was made well before than the term “superfluid” had been introduced by P. Kapitza<sup>46</sup>). Here we briefly consider this problem in direct comparison with results of Sec. 5 concerning to the hydrogen-hydrogen interaction.

### 6.1. Hamiltonian

The couple of two interacting  $^4\text{He}$  atoms ( $^4\text{He}$  dimer) is quite analogous to the hydrogen-hydrogen system (Fig. 2) except of the charges of the nuclei equal to  $Z_0 = 2$  and a pair of electrons is “prescribed” to each nucleus (for example, we suggest that electrons  $a$  and  $b$  belong to the first nucleus, and electrons  $c$  and  $d$  belong to the second one).

Within the Born-Oppenheimer-Heitler-London approximation the Hamiltonian of the system in the two-center form can be written as (cmp. with Refs. 7, 8, and 10, and 32)

$$\hat{H}_{\text{tot}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0) = \hat{H}_1(\mathbf{r}_a, \mathbf{r}_b) + \hat{H}_2(\mathbf{r}_c, \mathbf{r}_d) + \hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0) + \hat{H}_{\text{rel}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0), \quad (72)$$

where  $\hat{H}_1(\mathbf{r}_a, \mathbf{r}_b)$  and  $\hat{H}_2(\mathbf{r}_c, \mathbf{r}_d)$  are Hamiltonians of independent helium atoms (in this case  $Z_0 = 2$ ),

$$\hat{H}_1(\mathbf{r}_a, \mathbf{r}_b) = -\frac{1}{2}\Delta^{(e_a)}(\mathbf{r}_a) - \frac{1}{2}\Delta^{(e_b)}(\mathbf{r}_b) - \frac{Z_0}{r_a} - \frac{Z_0}{r_b} + \frac{Z_0}{|\mathbf{r}_a - \mathbf{r}_b|} \quad (73)$$

and

$$\hat{H}_2(\mathbf{r}_c, \mathbf{r}_d) = -\frac{1}{2}\Delta^{(e_c)}(\mathbf{r}_c) - \frac{1}{2}\Delta^{(e_d)}(\mathbf{r}_d) - \frac{Z_0}{r_c} - \frac{Z_0}{r_d} + \frac{Z_0}{|\mathbf{r}_c - \mathbf{r}_d|} \quad (74)$$

the Hamiltonian  $\hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0)$  is mutual interaction,

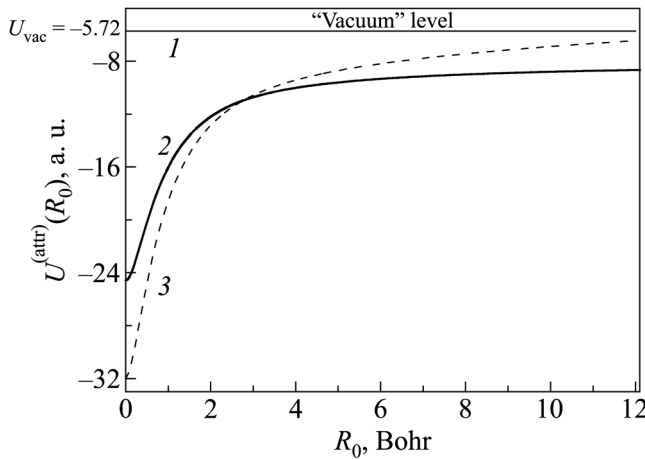
$$\hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0) = +\frac{Z_0^2}{R_0} - \frac{Z_0}{|\mathbf{r}_a - \mathbf{R}_0|} - \frac{Z_0}{|\mathbf{r}_b - \mathbf{R}_0|} - \frac{Z_0}{|\mathbf{r}_c - \mathbf{R}_0|} - \frac{Z_0}{|\mathbf{r}_d - \mathbf{R}_0|} + \frac{1}{|\mathbf{r}_d - \mathbf{R}_0|} + \frac{1}{|\mathbf{R}_0 + \mathbf{r}_c - \mathbf{r}_a|} + \frac{1}{|\mathbf{R}_0 + \mathbf{r}_d - \mathbf{r}_a|} + \frac{1}{|\mathbf{R}_0 + \mathbf{r}_c - \mathbf{r}_b|} + \frac{1}{|\mathbf{R}_0 + \mathbf{r}_d - \mathbf{r}_b|}, \quad (75)$$

and  $\hat{H}_{\text{rel}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0)$  is the relativistic (spin-orbit and spin-spin) part of interaction, which will be considered below. In fact,  $\hat{H}_{\text{rel}}^{\hat{\sigma}}$  is a real small corrections, proportional to the small parameter  $\alpha^2/4 \simeq 4.2$  K, where  $\alpha = 1/137$  is Sommerfeld (fine structure) constant.<sup>18</sup> As it can be seen from Eq. (75), we do not include into  $\hat{H}_{\text{int}}$  the  $R_0$ -independent interelectron repulsion within the pairs  $a-b$  and  $c-d$  which suppose to be prescribed to the first and second nucleus separately and are the parts of their own intrinsic (“vacuum”) energy.

### 6.2. Non-relativistic He-He interaction

The next step in our consideration is dividing the complete potential energy within helium dimer to attractive and repulsive part as it was made above for hydrogen-hydrogen system. The procedure is quite analogous to the scheme outlined in the previous section, and here we only show the result without describing the details of routine calculations. The attractive part of the He-He interaction is presented on Fig. 8. The curve 1 is the “vacuum” level of the system  $U_{\text{vac}} = -5.72$  a.u. (which is the total ground state energy  $U_{GS} \simeq 2.86$  a.u. of two independent spinless  $^4\text{He}$  atoms<sup>14</sup>).



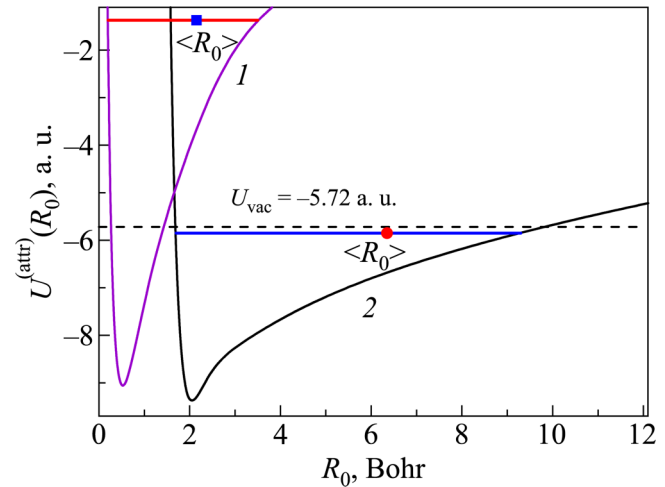


**FIG. 8.** Attraction part  $U^{(attr)}(R_0)$  of the total energy  $U(R_0)$  of the  $\text{He}_2$ -dimer as function of  $R_0$ : energy of two isolated spinless helium atoms in the ground state (“vacuum” level  $U_{\text{vac}} = -5.72$  a.u. which is the ground state energy of two independent  $^4\text{He}$  atoms<sup>44</sup>) (1); the spectrum calculated with the basis Eq. (35) of  $N_{\text{bas}} = 25$  elements ( $U^{(attr)}(0) = -24.60403$  a.u.) (2); the Padé extrapolated spectrum  $U^{(attr)}(R_0)$  of the attractive part in the limit  $N_{\text{bas}} \rightarrow \infty$  ( $U^{(attr)}(0) = -32.0$  a.u.) (3).

The curve 2 presents the ground state energy of  $^4\text{He}_2$ -dimer calculated with the basis Eq. (35) of  $N_{\text{bas}} = 25$  elements ( $U^{(attr)}(0) = -24.60403$  a.u.), whereas in reality this value must be equal to  $U^{(attr)}(0) = -(2Z_0)^2 \times 4 = -32.0$  a.u. In this connection, the curve 3 shows the Padé extrapolated spectrum  $U^{(attr)}(R_0)$  of the attractive part in the limit  $N_{\text{bas}} \rightarrow \infty$  which will be used below for further considerations.

After expansion procedure described in subsection 5.2 we get two potentials wells corresponding to  $R_0 \rightarrow 0$  (left well on Fig. 9) and to  $R_0 \rightarrow \infty$  (right well on Fig. 9) in qualitative analogy to the case of hydrogen-hydrogen interaction (Sec. 4) but with the peculiarities specific just to He–He system. As it can be seen from comparison between Fig. 6 and Fig. 9, the right well for helium is deeper than the left one (in the case of hydrogen the right well is, in fact, insufficient), but, more importantly, it is much broader and evidently nonharmonic. As a result, the inherent ground level of the left well (red level on Fig. 9) lies much higher than the vacuum level  $U_{\text{vac}} = -5.72$  a.u., whereas the corresponding level of the right well (blue level on Fig. 9) is only rough approximately 50 K below the  $U_{\text{vac}}$ . Exact numerical data cannot be produced within the developed approach in view of, at least, two reasons:

- the curves 1 and 2 on the Fig. 9 are divergent asymptotics obtained for immobile nuclei (the internuclear distance  $R_0$  is not accounted as dynamical variable of the problem, but only free parameter in the Schrödinger equation);
- the potential curves specified in a numerical form give no way to extract properly an effect of several Kelvins in magnitude against a vacuum background of several atomic units. Thus, we can conclude, that the energy of the bound state for  $^4\text{He}_2$ -dimer is extremely low and in this connection some



**FIG. 9.** The total interaction energy calculated with short-range repulsion asymptotics Eq. (66) for  $\text{He}_2$ -dimer. The “intrinsic” level in the short-range well is  $-1.37$  a.u. with  $\langle R \rangle = 2.1$  Bohr (1). The total interaction energy calculated with long-range repulsion asymptotics Eq. (68) for  $\text{He}_2$ -dimer (2). The “intrinsic” level in the long-range well is  $-5.85$  a.u. with  $\langle R_0 \rangle = 6.35$  Bohr  $\approx 3.36$  Å which is in good agreement with known molar volume of  $^4\text{He}$ <sup>44</sup> (see text). The dashed line corresponds to the “vacuum” level  $U_{\text{vac}} = -5.72$  a.u. which is the ground state energy of two independent  $^4\text{He}$  atoms<sup>44</sup>.

formally small relativistic corrections (of order  $\sim 1/c^2$ ) should play an essential role in the total balance of interactions in quantum helium matter.

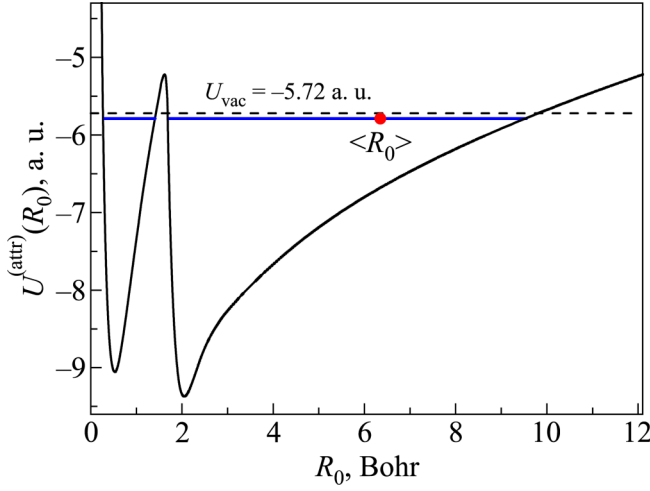
Of course, all the mentioned features in full measure are specified to the total potential dependence of Fig. 10 combined of the curves 1 and 2 from Fig. 9 [cmp. with Fig. 7(a)]. The barrier on Fig. 10 is much lower than in the case of hydrogen atoms [Fig. 7(a)], so that it can not change essentially the value of the level except of possibly splitting of order 5 K. In addition, the average interatomic distance in the well of Fig. 10 can be estimated as  $\langle R_0 \rangle = 6.35$  Bohr  $\approx 3.36$  Å which is in good agreement with molar volume  $\sim 28$  cm<sup>3</sup>/mol known for  $^4\text{He}$  liquid.<sup>44</sup> Under external pressure the barrier is lowered down the well and the ground state level becomes lower, so that helium transfers into solid phase. Anyway, despite the semi-quantitative approach used in the above-mentioned considerations, we can see that all the estimated values are in good agreement with experimentally obtained data for helium liquid.

The barrier on the potential curve of  $^4\text{He}$ – $^4\text{He}$  interaction was first discussed in review of R. A. Buckingham<sup>47</sup> and supported by a number of calculations.<sup>48–52</sup>

### 6.3. Spin-dependent interaction

The difference in observable physical properties between condensed phases of two helium isotopes testifies undoubtedly that different spin subsystems of  $^3\text{He}$  and  $^4\text{He}$  are principal background of interatomic interactions in the mentioned substances. Here we consider in some details only  $^4\text{He}$  with nuclear spin equal to zero. In this case the spin-dependent relativistic corrections of order  $\sim 1/c^2$





**FIG. 10.** The total interaction energy combined of the curves 1 and 2 from Fig. 9. The ground state of the system (blue level) is approximately  $\sim 50$  K lower than the “vacuum” level  $U_{\text{vac}} = -5.72$  a.u. (dashed line), for details see text.

are really small perturbation with a measure of the coefficient  $\alpha_s^2/4 \sim 4.2\text{K}$  (where  $\alpha_s = 1/137$  is Sommerfeld constant). In this connection, for simplicity, the interelectronic interaction of the required relativistic Hamiltonian  $\hat{H}_{\text{rel}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0)$  can be written in the limit  $R_0 = 0$  which just corresponds to condensed helium phase. This Hamiltonian includes only four electron coordinates  $\mathbf{r}_s$  (originate from the point  $R_0 = 0$ ) with four electronic spins  $\hat{\sigma}_s (s = a, b, c, d)$  of two helium shells and can be written as the superposition of spin-orbital  $\hat{H}_{\text{SO}}^{\hat{\sigma}}$  and spin-spin  $\hat{H}_{\text{SS}}^{\hat{\sigma}}$  contributions,<sup>10,16,32</sup>

$$\hat{H}_{\text{rel}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0) = \hat{H}_{\text{SO}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0) + \hat{H}_{\text{SS}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d). \quad (76)$$

Here

$$\begin{aligned} \hat{H}_{\text{SO}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d|\mathbf{R}_0) = & -i \frac{Z_0 g_s \alpha_s^2}{4} \left\{ \sum_s \hat{\sigma}_s \left[ \frac{\mathbf{r}_s}{r_s^3} \times \nabla_s \right] \right. \\ & + \sum_s \hat{\sigma}_s \left[ \frac{\mathbf{r}_s - \mathbf{R}_0}{|\mathbf{r}_s - \mathbf{R}_0|^3} \times \nabla_s \right] \\ & \left. - \frac{1}{Z_0} \sum_s \hat{\sigma}_s \sum_{s' \neq s} \left[ \frac{\mathbf{r}_{ss'}}{r_{ss'}^3} \times (\nabla_s - \nabla_{s'}) \right] \right\}, \quad (77) \end{aligned}$$

where  $r_{ss'} = r_s - r_{s'}$ ,  $g_s = 1.001145$  is spin  $g$ -factor, and  $\hat{\sigma}$  is the vector with components built of Pauli matrices. Furthermore, the spin-spin part is

$$\begin{aligned} \hat{H}_{\text{SS}}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) = & \frac{g_s^2 \alpha_s^2}{4} \left\{ -\frac{8\pi}{3} \sum_{s' \neq s} \hat{\sigma}_s \hat{\sigma}_{s'} \delta(\mathbf{r}_{ss'}) \right. \\ & \left. + \sum_{s \neq s'} \frac{1}{r_{ss'}^3} \left[ \hat{\sigma}_s \hat{\sigma}_{s'} - 3 \frac{(\mathbf{r}_{ss'} \cdot \hat{\sigma}_s)(\mathbf{r}_{ss'} \cdot \hat{\sigma}_{s'})}{r_{ss'}^2} \right] \right\}. \quad (78) \end{aligned}$$

To obtain the spin density matrix for our problem, we have to calculate the average  $\langle \text{GS} | \hat{H}_{\text{rel}}^{\hat{\sigma}} | \text{GS} \rangle$  over the spatial ground state of the four-electron system on the  $^4\text{He}-^4\text{He}$  interatomic bond, and as the ground state wave function we choose

$$|\text{GS}\rangle = |100\rangle_a |100\rangle_b |100\rangle_c |100\rangle_d.$$

In this case, due to symmetry reasons, the matrix elements of  $\langle \text{GS} | \hat{H}_{\text{SO}}^{\hat{\sigma}} | \text{GS} \rangle$  are equal to zero, and the spin density matrix has the form

$$\begin{aligned} \rho(\hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c, \hat{\sigma}_d | R_0) = & \langle \text{GS} | \hat{H}_{\text{SS}}^{\hat{\sigma}} | \text{GS} \rangle \\ = & \frac{g_s^2 \alpha_s^2}{4} \left\{ -\frac{8\pi}{3} \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'} \langle \text{GS} | \delta(\mathbf{r}_{ss'}) | \text{GS} \rangle \right. \\ & + \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'} \left\langle \text{GS} \left| \frac{1}{r_{ss'}^3} \right| \text{GS} \right\rangle \\ & \left. - 3 \left\langle \text{GS} \left| \frac{(\mathbf{r}_{ss'} \cdot \hat{\sigma}_s)(\mathbf{r}_{ss'} \cdot \hat{\sigma}_{s'})}{r_{ss'}^5} \right| \text{GS} \right\rangle \right\}. \quad (79) \end{aligned}$$

It is reasonable to suggest that magnetic moments of the four electrons on the common interatomic bond will be oriented preferable perpendicular to this bond, it means that  $\mathbf{r}_{ss'} \cdot \hat{\sigma}_s \simeq 0$ , and last term in Eq. (79) can be omitted. As a result we have (cmp. with Ref. 32)

$$\rho(\hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c, \hat{\sigma}_d | R_0) = \mathcal{E}_1(R_0) + \frac{J}{2} \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'}, \quad (80)$$

where  $\mathcal{E}_1(R_0)$  is the energy of the ground state, and  $J$  is the magnitude of spin-spin pair exchange (Heisenberg exchange constant) represented through the corresponding spatial matrix elements,

$$\begin{aligned} J = & \frac{g_s^2 \alpha_s^2}{4} \left\{ -\frac{8\pi}{3} \langle \text{GS} | \delta(\mathbf{r}_{ss'}) | \text{GS} \rangle + \left\langle \text{GS} \left| \frac{1}{r_{ss'}^3} \right| \text{GS} \right\rangle \right. \\ & \left. - 3 \left\langle \text{GS} \left| \frac{(\mathbf{r}_s - \mathbf{r}_{s'})^2}{3r_{ss'}^5} \right| \text{GS} \right\rangle \right\}. \quad (81) \end{aligned}$$

Whereas the energy of the spatial ground state can be calculated with high enough accuracy,<sup>10,32</sup> the calculation of  $J$  needs estimation of the matrix elements with Coulomb irregularities which must be renormalized using a certain procedure of quantum electrodynamics.<sup>33</sup> This procedure is rather complicated, and here we restrict the consideration to the simplest qualitative reasons. In 1930 E. Fermi proposed an approach<sup>53</sup> which allowed to get an estimation for the spatial matrix element  $\langle r_{ss'}^{-3} \rangle$ , and here we use some similar procedure. We use the simplest ground state wave function Eq. (57) with  $a_{11}(R_0) = 1$  and  $a_{ij}(R_0) = 0$  for  $i, j \neq 1$  (see also Ref. 14),

$$|\text{GS}\rangle = 2\alpha \exp[-\alpha(r_s + r_{s'})],$$

where  $\alpha = Z_0 - \sigma$ , and  $\sigma$  is screening constant,<sup>18,28</sup> the corresponding calculations for helium atom<sup>14</sup> give  $\sigma \simeq 0.2323$  (in Refs. 29 and 31) are known other estimations of  $\sigma \simeq 0.3125$ ). Then we calculate

exactly the matrix element (cmp. with Ref. 14),

$$\gamma = \left\langle \text{GS} \left| \frac{1}{r_{ss'}} \right| \text{GS} \right\rangle = \frac{13}{16} \alpha = \frac{13}{16} (Z_0 - \sigma), \quad (82)$$

and suppose for estimation that

$$\left\langle \text{GS} \left| \frac{1}{r_{ss'}} \right| \text{GS} \right\rangle \sim \gamma^3 = \left( \frac{13}{16} (Z_0 - \sigma) \right)^3 \quad (83)$$

and, correspondingly,

$$\left\langle \text{GS} \left| \frac{(\mathbf{r}_s - \mathbf{r}_{s'})^2}{3r_{ss'}^5} \right| \text{GS} \right\rangle \sim \frac{2}{3} \left( \frac{13}{16} \right)^5 (Z_0 - \sigma)^3. \quad (84)$$

The matrix element with  $\delta$ -function (contact interaction, see also Ref. 54) allows formally exact calculation with use of the corresponding representation,<sup>27</sup>

$$\frac{8\pi}{3} \langle \text{GS} | \delta(\mathbf{r}_a - \mathbf{r}_b) | \text{GS} \rangle = \frac{1}{3} (Z_0 - \sigma)^3. \quad (85)$$

And, finally, in this approximation the spin-orbit contribution is equal to zero. As a result,

$$J = \frac{\alpha_s^2}{4} (Z_0 - \sigma)^3 \left[ -\frac{1}{3} + \left( \frac{13}{16} \right)^3 - 2 \left( \frac{13}{16} \right)^5 \right] \simeq -11.716 \text{ K}. \quad (86)$$

Note, that this value is just the depth of the Lennard-Jones potential well for helium.<sup>55</sup> Spectrum  $\mathcal{E}_i^{(s)}$  of the spin density matrix Eq. (80) has been presented in Table IV.

The spin spectrum  $\mathcal{E}_i^{(s)}$  consists of three degenerate levels with quintuply degenerate ground state  $\mathcal{E}_1^{(s)} = 6J = -70.3 \text{ K}$ . The spin-spin interaction lowers the bound energy  $\mathcal{E}_1(R_0)$  on the He–He interatomic bond and at  $T \rightarrow 0$  stabilizes a helium condensed phase near the labile equilibrium level of spatial bond presented on Fig. 10.

Thus, the spin contribution to the interatomic interaction in condensed helium phases seems to be presented in the standard Heisenberg form<sup>32</sup>

$$\hat{H}_{\text{spin}} = \frac{J(R_0)}{2} \sum_{\mathbf{f}, \delta} \left[ \hat{\sigma}_{\mathbf{f}}^{(a)} \hat{\sigma}_{\mathbf{f}}^{(b)} + \hat{\sigma}_{\mathbf{f}}^{(a)} \hat{\sigma}_{\mathbf{f}+\delta}^{(a)} + \hat{\sigma}_{\mathbf{f}}^{(a)} \hat{\sigma}_{\mathbf{f}+\delta}^{(b)} + \hat{\sigma}_{\mathbf{f}}^{(b)} \hat{\sigma}_{\mathbf{f}+\delta}^{(a)} + \hat{\sigma}_{\mathbf{f}}^{(b)} \hat{\sigma}_{\mathbf{f}+\delta}^{(b)} + \hat{\sigma}_{\mathbf{f}+\delta}^{(b)} \hat{\sigma}_{\mathbf{f}+\delta}^{(b)} \right], \quad (87)$$

where  $\delta$  is a unit vector directed to the corresponding nearest

TABLE IV. Spin states within  ${}^4\text{He}$ – ${}^4\text{He}$  bond.

State	Energy, $\mathcal{E}_i^{(s)}/J$	Parity	Deg.
1	−6	even	5
2	2	odd	9
3	6	even	2

neighbor from the first coordination sphere of the site  $\mathbf{f}$  ( $a$  and  $b$  denote electrons prescribed to the site  $\mathbf{f}$ ). Thus, each bond with the neighboring atom from the first coordination sphere contains four spins bonded by mutual exchange of spin pairs and four-spin exchange. The exchange constant  $J(R_0)$  depends on interatomic distance  $R_0$  and, hence, on mutual displacements of sites. It is the mechanism of spin-phonon interaction in the spin-ordered He II phase. Phonons or external periodic sound waves produce a gradient of sites displacements and, as a result, becomes a periodic magnetization proportional to this gradient. The alternative magnetization is a curl of electric field (Faraday law, electromotive force), and it could be an explanation for Rybalko effect of electric induction in the wave of second sound.<sup>56,57</sup>

Another fact to be taken into account is spin-orbital splitting. Spin-orbital contribution [Eq. (77)] in view of symmetry reasons has a rather small value in the ground state, but due to explicit dependence on  $R_0$  it has a strong effect on spin-lattice (spin-phonon) coupling. Spin dynamics (with transformation properties of angular momentum) “loads” phonon modes, and this leads to the minimum in phonon spectrum just similar to the translation-rotation coupling in molecular crystals.<sup>58</sup>

## 7. DISCUSSION

It is well known that the law of nature says: all perfect gases (the gases of low enough density where we can mainly neglect by long-range interatomic interaction), being injected into an empty volume, fill up this volume uniformly. It is possible only at interatomic repulsion in the perfect gas. However, if the perfect gas is preliminary compressed above some temperature-dependent critical pressure and then admitted quasi-stationary into empty volume (gas throttling), then it will be separated into dense liquid phase and the corresponding saturated vapor which can be interpreted again as a perfect gas. It means (in the complete agreement with our result presented in Fig. 10) that, to be condensed, a real gas must be compressed and cooled within a Joule-Thomson process,<sup>59,60</sup> and the state of interatomic interaction in this gas must be transferred through the barrier to the left potential well of Fig. 10 (quantum-mechanical calculations of Fig. 10 correspond to the temperature  $T = 0$ ). In other words, the process can be considered as follows. If a perfect gas is compressing along a subcritical Van der Waals (VdW) isotherm ( $T < T_c$ ) from a certain initial pressure  $p_0$  and the corresponding specific volume  $V_0(p_0, T)$  then it remains a monophasic substance with rather great average interatomic distances  $\langle R_0 \rangle$  (this corresponds to the right well on Fig. 10) until the volume  $V$  of the gas becomes the specific value  $V_i$  which corresponds to the phase transformation into two-phase system where the gaseous substance decays into coexisting dense condensate (with  $\langle R_0 \rangle$ ) according to the left well on Fig. 10 and low-density saturated vapor (with large  $\langle R_0 \rangle$ ) of the right well on Fig. 10). To fall in the first-order phase transition the system needs to possess a piece of latent heat of transition, i.e., energy that would be expended for penetrating through the barrier between wells on Fig. 10), and this energy is due to the external work carried on the compression within the Joule-Thomson process.

The potential well qualitatively analogous to the curve of Fig. 10 was considered by R. A. Buckingham in the review paper of

1961 (see Ref. 47, Figs. 1–3 from this paper and literature cited therein). It should be noted that in literature of that times the interatomic interaction in helium was considered exclusively as repulsion<sup>29,30,61–63</sup> and is quite evident given problems of gaseous kinetics which were actually within the 50s and 60s of twenty century. More detailed attention to the attractive part of interaction, especially in helium, was payed later for reasons of condensed matter physics, among them for clarification of superfluid and supersolid phenomena.

The results of the Sec. 6 show that the presence of the potential barrier between the deep (but comparable narrow) left well and the much wider right-hand well can be a reason for existence within the left well of long-leaving metastable bound states with energy even a bit higher than the vacuum level of  $\sim -5.7$  a.u., and these states correspond to the boiling phase liquid He I. Below 2.17 K the system has been stabilized by contribution from the spin subsystem, and we have the He II phase with smooth and calm surface (Shubnikov<sup>45</sup> determined He II phase as “liquid crystal”).

The character of interatomic interactions is known as a central physical problem in the theory of condensed molecular systems (especially low-temperature systems like quantum liquids and crystals). The crucial moment of the corresponding problem is the role of so-called Van der Waals forces which are suggested to be intermolecular attraction with potential energy  $U_{VdW}(R_0) \sim 1/R_0^6$  (where  $R_0$  is intermolecular distance). At the first time the mentioned forces were introduced by J. D. Van der Waals<sup>64</sup> in his famous VdW equation of state for “real” gas of  $N$  molecules occupied the volume  $V$ ,

$$\left(p + \frac{a}{V^2}\right)(V - b) = Nk_B T, \quad (88)$$

where additional intrinsic pressure  $a/V^2$  (over external pressure  $p$ ) exists due to certain attraction forces among molecules of a gas with high enough density. The standard “explanation” of  $\sim 1/R_0^6$ -law is a claim that the  $\sim a/V^2$  term is consequently proportional to  $\sim L^{-6}$ , where  $L$  is a linear size of the system in volume  $V \sim L^3$ . However, we can see that  $a/V^2 \sim L^{-6}$  is not the energy but the pressure, i.e., the force applied to the whole thermodynamic system restricted in volume  $V$ . Thus, if the force is  $\sim +L^{-6}$  –dependent (the overpressure tends to compress the system), then the energy of interaction must be intermolecular attraction  $U \sim -L^{-5}$ . This simplest conclusion is completely supported by our calculation of quadruple-quadruple interaction within the first order perturbation theory [see Sec. 4, Eq. (40)].

In this connection the intrinsic pressure  $a/V^2$  can not be considered as a direct result of mutual interaction between all the  $N(N-1)/2$  possible pairs of individual molecules in the real gas, but only as of the equilibrium thermodynamic parameter (as the corresponding thermodynamic average) of the many-particle system as a whole, and, consequently, the VdW parameters  $a$  and  $b$  must be, at least, temperature-dependent, as we can see this from the real experimental data.<sup>55</sup> This fact is realized when deriving the VdW equation from the rigorous virial expansion,<sup>59,60</sup> of the gas partition function, and, as a result, the VdW coefficient  $a$  in Eq. (88) is the second virial

coefficient of the corresponding expansion,

$$a(T) = \frac{1}{2} \int \left[ 1 - \exp\left(-\frac{U_{1,2}(R_0)}{T}\right) \right] dV, \quad (89)$$

where  $U_{1,2}(R_0)$  is the potential energy of the pair intermolecular interaction. It is noticeable that the thermodynamic approach does not determine the spatial dependence of the potential function  $U_{1,2}(R_0)$  in the integrand of Eq. (89). To derive the equation Eq. (88) we need only postulate the  $N(N-1)/2$  pair attractions within a system of  $N$  molecules<sup>60</sup> and suggest an acceptable form of  $U_{1,2}$  to enable convergence of the functional Eq. (89).

The first attempt to establish a form of  $U_{1,2}(R_0)$  from quantum mechanical principles was made by F. London<sup>65</sup> in 1930. He proceeded from the fact that atoms are not elementary particles, but polarized systems due to their own intrinsic degrees of freedom, and represented the potential function  $U_{1,2}(R_0)$  as an effective dipole-dipole interaction<sup>26</sup> proportional to  $\sim 1/R_0^3$ . The next step is to find the average of dipole-dipole interaction over the ground state. London suggested that wave function the ground state is a composition of the spherically symmetric electronic shells of unperturbed atoms, and then obtained the zero contribution in the “first order of perturbation theory” which is quite evident in view of incompatibility between symmetries of dipole-dipole term and ground state wave function of the chosen form. In this situation, if passing on to “second order perturbation theory”, then one can obtain the well-known  $\sim 1/R_0^6$ -dependence. Thus, since 1930 the problem of  $\sim 1/R_0^6$ -law is discussed as a master concept in the theory of intermolecular interactions and used as almost inevitable background for the most part of known popular models of atom-atom potentials.<sup>13,23,55</sup>

This result seems to be not quite correct for at least two reasons:

- (i) along with dipole-dipole interaction  $\sim 1/R_0^3$ , the multipolar expansion of the potential energy  $U(R_0)$  contains the interactions of the higher orders (dipole-quadrupole  $\sim 1/R_0^4$ , quadruple-quadruple  $\sim 1/R_0^5$ , etc.), and just quadruple-quadruple interaction  $\sim 1/R_0^5$  gives non-zero average in the first order of perturbation theory even if the first-order wave function has the London’s spherical symmetry relative to nuclei of non-perturbed atoms on the distance  $R_0$ ;
- (ii) the electronic shells of the interacting atoms cannot remain spherically symmetric due to mutual influence of their electromagnetic fields, and as a result, the “correct wave function of zero approximation” must have non-spherical two-center shape, which leads immediately to non-zero first-order dipole-dipole interaction  $\sim 1/R_0^3$  (for example, a complex of two mutually interacting electrically neutral atoms can be treated as excited diatomic molecule where atoms are bonded by dipole-dipole “dispersive” forces). The simplest physical conclusion is as follows: if at variation of  $R_0$  the atoms hold its spherically symmetric ground states independent on  $R_0$ , it means that the atoms do not “feel” each other, spherically symmetric shells do not possess any dipolar momenta, and dipole-dipole interaction is identically equal to zero within any order of perturbation theory.

The sophistic postulate of  $1/R_0^6$  attraction between a pair of gas particles is in obvious discrepancy with abovementioned well-known experimental fact of free expansion of perfect gases. The progressive extension of the perfect gas is possible only if the mutual interaction between gas molecules at rather large intermolecular distances (at low gas densities) is evidently repulsion. A frequently-used determination of an ideal gas as a system without interaction between particles<sup>59</sup> is not quite correct (let alone the gas without interaction does not contain the  $1/R_0^6$  attraction as well) because in the absence of any interaction the gas is unable to establish the thermodynamic equilibrium at given temperature and pressure inside a given volume. To make this determination more realistic we have to add the condition that intersection of phase trajectories of any particles in the coordinate subspace is forbidden (in other words the particles can not penetrate each other). It corresponds to so-called hard sphere model which leads in the classical case to the Tonks equation of state,<sup>66</sup>  $p(V - b) = Nk_B T$  (it just corresponds to the VdW equation of state Eq. (88) without attraction, i.e. at  $a = 0$  or  $V \rightarrow \infty$ ). The interaction  $U(r)$  in the system of hard spheres of radius  $r_s$  is

$$U(r) \begin{cases} +\infty & r < 2r_s, \\ 0 & r > 2r_s, \end{cases} \quad (90)$$

and it corresponds to the strong short-range repulsion of the otherwise completely independent isotropic objects of a finite size. In reality  $V \gg b$ , so that the Tonks equation becomes the proper equation of state,  $pV = Nk_B T$ , for the perfect gas.

A proper description of the interaction between two electrically neutral atoms in the non-relativistic approximation proposes the solution of many-electron Schrodinger equation with rigorous including of all electronic and nuclear spatial degrees of freedom (the intrinsic degrees, spins, produce small relativistic corrections of order  $1/c^2$ ) with exact account of static Coulomb pair interactions between all elements (electrons and nuclei) of the system. It means formally that all electrons are collectivized and we can no longer expect that anyone electron belongs to anyone nucleus, so that all equivalent particles are undistinguished. It is frequently assumed that in adiabatic (Born-Oppenheimer-Heitler-London) approximation at immobile nuclei the system can be described as an “interaction” of two independent atoms in its “ground states”. This sophistic establishment is physically untenable because in the right sense “interaction” means that each atom disturbs the other, and no longer individual ground state is possible but only the ground state of the diatomic complete system as a whole is physically reasonable. If atoms remain strongly in their ground states then the electronic distributions within the atomic shells is independent on the interatomic distance  $R_0$ , and they are simply impenetrable hard spheres with global repulsion in a manner of Eq. (90). The electronic indistinguishability means that the basis for the diatomic system [see Eq. (33)] must be built as direct composition of complete one-electron sets of states (but not only one-electron ground states as it assumes the London’s treatment). It means that the ground state of the complete system is combined principally of excited states of “individual” atoms. It is a physical background of the mutual atomic polarizability and the mechanism

of the real interaction between electrically neutral atoms. However, at the large distances the interaction is rather weak, and it can only slightly modify the unperturbed global repulsion (the interaction energy remains greater than the vacuum level  $U_{\text{vac}} = -1$  for hydrogen, and  $U_{\text{vac}} \simeq -5.7$  for helium, see Figs. 6, 7, 9, 10), but not change it radically until the distance between nucleus becomes rather small. This fact is clearly demonstrated by Fig. 7(a): the attraction becomes predominant only at  $R_0 < R_B$ .

The complete wave function for the system with nontrivial dipole-dipole interaction must contain the non-spherical components to take into account deformation of initially spherical atomic shells due to mutual polarization (of course, the deformation is  $R_0$ -dependent). In this case the electronic charge distribution is not spherically symmetric relative to each nucleus, but the system has a symmetry plane at the half of the internuclear distance,  $R_0/2$ , and perpendicular to the direction of  $\mathbf{R}_0$ . It means, that there are two associated local dipole momenta,  $\mathbf{d}_1$  and  $\mathbf{d}_2$ , on the distance  $R_0$ , and due to symmetry these momenta are strongly equal in magnitude and opposite in directions,  $\mathbf{d}_1 = -\mathbf{d}_2$ , so that the total dipole momentum of the system,  $\mathbf{D} = \mathbf{d}_1 + \mathbf{d}_2 = 0$  vanishes. On the other hand, the interaction energy between two dipole momenta,<sup>54,67</sup>

$$U = \frac{(\mathbf{d}_1 \mathbf{d}_2) - 3(\mathbf{n}_0 \mathbf{d}_1)(\mathbf{n}_0 \mathbf{d}_2)}{R_0^3}, \quad \mathbf{n}_0 = \frac{\mathbf{R}_0}{R_0} \quad (91)$$

with opposite orientation is anyway repulsion. Despite the non-spherical contribution to the ground state wave function at  $R_0 > 1$  is less than 10% and it vanishes at  $R_0 \rightarrow \infty$  as  $1/R_0^3$ , the dipole-dipole repulsion is the most slowly decreasing part of interaction (as compared, for instance, to quadruple-quadruple attraction  $\sim 1/R_0^5$ ), and just the interatomic repulsion survive at great distances  $R_0$  in agreement with data of Figs. 7 and 10. The dipole-dipole attraction could be possible only if the vectors  $\mathbf{d}_1$  и  $\mathbf{d}_2$  are parallel each other, but such a configuration is in contradiction with the conditions of the spatial symmetry of the system under study. If  $R_0$  decreases than quadruple-quadruple attraction  $\sim 1/R_0^5$  becomes predominant and standard Van der Waals situation is realized.

The principal importance of the spin subsystem for the rigorous model of the interatomic interaction in helium becomes more evident when comparing the  $^4\text{He}$  and  $^3\text{He}$  behavior in condensed phases.  $^4\text{He}$  demonstrates the  $\lambda$ -transition which is the phase transition from disordered simple liquid (He I) to specifically ordered “superfluid” phase (He II), whereas  $^3\text{He}$  remains simple liquid (completely disordered) up to very low temperature. The only difference between two isotopes is the nuclear spin of  $^3\text{He}$ . It means that two electronic spins of the  $^3\text{He}$  shell are affected by the magnetic field from the nuclear magnetic moment (hyperfine splitting). As a result, this influence destroys the exchange interaction among electronic spins on the interatomic bond and, hence, the possible ordering in the electronic spin subsystem as a whole (nuclei and electrons are non-equivalent particles). L. Shubnikov<sup>45</sup> for the first time called the attention to an evident analogy between the  $\lambda$ -point anomaly in He II “similar to that shown by ferromagnetic bodies at the Curie point”<sup>45</sup> and the corresponding anomaly in crystalline substances caused by “change of order in the crystal”.<sup>45</sup> In this paper Shubnikov interpreted the He II phase as liquid crystal built of an array of small anisotropic crystallites



arranged into easily deformable substance (“liquid crystal”). Unfortunately, that time they did not manage to find the optical effects typical for anisotropic crystalline lattices. The unsucces in these experiments could be caused by the extremely small polarizability of the helium atom, and, possibly, when studying the ordering in He II, it is reasonable to pay attention in future to magnetic response of the  $^4\text{He}$  spin subsystem. However, in the modern researches of He II, it was discovered that small droplets of the He II phase have got a finite contact angle with substrate (not spreading along the surface) even if the substrate is known to be completely wetted by the helium liquid.<sup>68</sup> It means that in small droplets the He II phase exists in a form of ice-like crystallites in the full agreement with above-mentioned Shubnikov’s conclusion.<sup>45</sup> In this connection the “superfluidity” of He II can be considered as superplasticity or yield properties of the liquid crystal with specific spatial ordering. There are many experimental facts (above all obtained from a great number of experiments on inelastic neutron scattering<sup>69</sup>) which support this conclusion.

Thus, undergo from phase He I to phase He II can be associated with a certain spatial ordering due to effects of spin subsystem with Hamiltonian (87). The exchange constant  $J$  depends on interatomic distance  $R_0$  and, hence, on mutual displacements of sites. It is the mechanism of spin-phonon interaction. The periodic sound waves (phonons or external acoustic excitation) with gradient of sites displacements are associated with periodic magnetization proportional to this gradient. The alternative magnetization is a curl of electric field (Faraday law, electromotive force), and it could be an explanation for Rybalko effect of electric induction in the wave of second sound.<sup>56,57</sup>

Of course, it is reasonable to suggest that the transformation from phase He I to phase He II ( $\lambda$ -transition) is due to transformation in the spin subsystem. As it seen from Table IV, the ground state of the four-spin subsystem on the He–He bond makes the completed ground state of approximately 70 K lower as compared to the energy of the bare electronic value (see Tables I and II). At low temperature the low-energy spin-spin and spin-phonon interactions<sup>10</sup> are of fundamental importance. The fivefold degenerated ground state will be split through small (of order 2–5 K)  $R_0$ -dependent spin-orbit interaction, linear on spin operators  $\hat{\sigma}$  [see Eq. (77)]. However, to solve this part of the problem we have to calculate properly the matrix elements of the Hamiltonians  $\hat{H}_{SS}^{\sigma}$  and  $\hat{H}_{SO}^{\sigma}$ . The well-known difficulties on this way are Coulomb irregularities of the corresponding matrix elements which should be canceled with an approach used in quantum electrodynamics.<sup>33</sup> Realization of the corresponding program will make us possible not only calculate proper the spin exchange parameters, but also establish the features of spin-phonon interaction in condensed helium phases. This program will be the subject of further investigations.

The ordering in the spin subsystem of the He II phase means inevitable spatial ordering in the helium interatomic structure because all spins are property of electrons which are strongly correlated within atomic shells and, moreover, within a common valence bond of the condensed phase. For instance, the stable atomic configuration of He II phase can be built as a stack of 2D closely packed atomic planes on triangular lattice. Within the plane each atom has six mutual bonds with nearest neighbors from the first coordination sphere. The mentioned planes can be packed into a

stack of the planes without breaking the closest packing principle (so-called polytypic structure,<sup>70,71</sup> see also books).<sup>72,73</sup> Each atom from the close-packed plane has only three mutual bonds with atoms from upper and lower neighboring planes, so that interplane connection is a half weaker as compared to in-plane one. As a result, the stack is unstable relative to easy glide between planes in stack, and this mechanism has the close relation to the layered model of superfluid liquid.<sup>74</sup> The polytype remains ordered relative to arbitrary in-plane direction, whereas in perpendicular direction it can be completely disordered (chaotic stacking fault phase).<sup>72</sup> Under external pressure of approximately 25 bar the polytype of  $^4\text{He}$  transforms into hexagonal close-packed crystal, and this fact is an evidence of the pressure effect on the interatomic interaction in helium condensed phases.

## 8. CONCLUSIONS

- (1) If two electrically neutral atoms spaced with distance  $R_0 < \infty$  interact each other then these atoms can no longer remain in their “individual” ground states. If the atomic “ground states” remain unchanged under changes of  $R_0$ , it means that atoms do not feel each other at all, and there is no mutual interaction between them. Thus, the basis constructed of the ground state wave functions of independent atoms can not be used for development of the proper perturbation theory, but only for rather approximate variational approach. Mutual interaction means that there are no longer “individual” atoms but the diatomic system “as a whole”, so that the rigorous procedure must be based on the basis constructed as a direct composition of all the possible states of the separate atoms. The interatomic distance  $R_0$  is a dynamical variable and must be incorporated into Schrodinger equation on equal terms as standard degree of freedom. The Born-Oppenheimer-Heitler-London model excludes the internuclear motion from the common quantum mechanical problem and restricts the real picture of interaction among electrons and protons within a closed atom-atom system.
- (2) In a general sense, the potential energy of electromagnetic interaction between elementary charged particles (electrons and protons) in any non-relativistic Schrodinger equation can not be considered as a certain “perturbation” in view, at least, two reasons: (i) the electrostatic Coulomb interaction is represented by harmonic functions which do not contain any really small parameter to develop the proper perturbation procedure (magnetic part proportional to  $1/c^2$  are the really small relativistic corrections which need be prepared with Pauli equation); (ii) each electrostatic interaction  $\sim |\mathbf{r}_a - \mathbf{r}_b|^{-1}$  contains the integrable singularity at  $\sim |\mathbf{r}_a - \mathbf{r}_b| = 0$  which define principally the character of solution of the linear Schrodinger equation, but any “perturbation” procedure destroys the real behavior in the vicinity of the irregular points, and as a result, the exact solution will be replaced by an asymptotic estimation with noncontrolled accuracy.
- (3) Even simple London-like estimation shows that there is a leading quadruple-quadruple attraction  $\sim -R_0^{-5}$  within the first order approximation, instead of usually believed  $\sim -R_0^{-6}$  of second order. The  $\sim -R_0^{-5}$  attraction law is in direct agreement

with phenomenological postulate of Van der Waals equation of state and second virial coefficient approximation in statistical physics.

- (4) The proper solution of the corresponding Schrodinger equation shows that the interaction between two electrically neutral atoms at large interatomic distances is evidently repulsion. This result is in good agreement with the obvious fact that any perfect gas (a gas of low enough density) introduced into empty volume fills up the one uniformly. Another experimental fact is existence of stable interphase boundary between dense liquid (or solid) phase and its dilute saturated vapor. In the global sense this result clarifies the fact that within Universe the hydrogen exists in simple monoatomic repulsive form (which supports by experimentally registered hyperfine splitting response with wavelength  $\lambda = 21$  cm) at low enough densities, and it can explain the physical nature of the global expansion of the Universe. Thus, the interstellar atomic hydrogen isotopes (and, certainly, helium isotopes) can serve as real candidates on the role of hypothetical repulsive “dark matter” whose estimated density is quite equal to the density of protons (or, the same, hydrogen atoms) within the interstellar material. Note, that anyway a proper solution of the Schrodinger equation for interatomic interactions at long distances must be based not only on the basis of discrete spectrum, but also on the continuous spectrum of scattering states.<sup>41</sup>
- (5) The explanation of the London’s sophism lies in the incorrect use of a dipolar-free spherically symmetric basis (as composition of unperturbed spherically symmetric ground states of independent atoms) to calculate the dipole-dipole part of intermolecular interaction. Of course, in this connection the first-order matrix element of dipole-dipole interaction is found to be equal to zero, because of evident incompatibility between symmetries of the applied trial function and the dipolar term in the expansion of the potential energy over reciprocal powers  $R_0^{-n}$  of the intermolecular distance. The real dipole-dipole contribution as a part of the total interatomic interaction is repulsion  $\sim 1/R_0^3$ . It can be obtained within the “first order perturbation theory” only with use the correct wave functions of the first order which take into account correctly the real symmetry of the problem.
- (6) The interatomic distance  $R_0$  is a dynamical variable and must be incorporated into Schrodinger equation on equal terms as standard degree of freedom to obtain the real value of bonding energy between electrically neutral atoms. In the most interesting case of  $^4\text{He}$ - $^4\text{He}$  interaction we get the coarse non-relativistic estimation of this value of order  $\sim 10 - 100$  K, but this estimation has been produced on the basis of two heteropolar asymptotics (at  $R_0 \rightarrow 0$  and at  $R_0 \rightarrow \infty$ ) stitched in an intermediate point  $0 \leq R_0 < \infty$  of the  $R_0$ -axis. Anyway, this result allows us to conclude that (i) the bound state of helium atoms (probable unstable) with bonding energy of several Kelvins exists creating the boiling He I liquid phase; (ii) the relativistic spin-spin part of interaction stabilized it into ordered He II phase where spin-phonon interaction plays a principal role in the observable properties of the  $^4\text{He}$  “superfluid” below  $\lambda$ -line. Two strongly correlated electronic spins within the

united  $^4\text{He}$  shell form the natural Cooper pair, and helium four below  $\lambda$ -line can be considered as spin-ordered phase like “spin-ice” of ordered Cooper pairs or, more exactly, as predicted by Shubnikov<sup>45</sup> “liquid crystal” based on spin-phonon coupling. The quintuply degenerate ground state of the spin subsystem is splitted due to relatively small spin-orbit coupling, and it is a nature of so-called “roton gap” in the phonon spectrum of the conventional model for the superfluid  $^4\text{He}$ . In  $^3\text{He}$  atom the magnetic field from one-half nuclear spin destroys the spin-spin correlation within a unitary electronic shell (hyperfine splitting), and then the spin ordering within the condensed helium phase is impossible until the nuclear spin ordering has been established at millikelvin temperature (superfluidity of  $^3\text{He}$ ).

- (7) The only difference between two helium isotopes is one-half nuclear spin of  $^3\text{He}$ , and only this circumstance is a nature of radical difference between observable physical properties of  $^4\text{He}$  and  $^3\text{He}$ . So, we can conclude that all the extraordinary properties of the He II phase are due to the self-organization of electronic spins within coupled electronic shells of neighboring  $^4\text{He}$  atoms. The presence of nuclear spin in  $^3\text{He}$  atom (and, hence, hyperfine disturbance which contribute mainly to the spin-lattice relaxation) destroys the ordering in the subsystem of electronic spins.
- (8) In the most practically important cases the detailed form of the pair interatomic potential is inessential for successful theoretical description of experimentally observed dynamic and thermodynamic phenomena in macroscopic condensed matter. It is enough to use some general properties of intermolecular interaction in the many-body systems.
- (9) At saturated vapor pressure in the temperature range  $T_\lambda < T < 4.2$  K ( $T_\lambda = 2.17$  K) the  $^4\text{He}$  condensate exists as a simple liquid without long range ordering. At temperature below  $\lambda$ -point the contribution of the ordered spin subsystem of  $^4\text{He}$  becomes dominating, and the He II phase can be interpreted as a spin-ordered system with exchange constant of approximately 12 K. The principal role of the spin subsystem in the observable properties of  $^4\text{He}$  is evident, when compare with corresponding features of  $^3\text{He}$ . The phase diagrams of the both isotopes are quite different, which means the difference in interatomic interactions in the corresponding condensed phases. However, the only difference between  $^3\text{He}$  and  $^4\text{He}$  is the nuclear spin of  $^3\text{He}$  as compared with zero-spin nucleus of  $^4\text{He}$ , and hence, we can see the effect of the tensor interaction between  $^3\text{He}$  nucleus and two-spin shell (electrons and nuclei are non-equivalent systems). It makes us possibility to conclude that only spin-spin and spin-phonon interactions and ordering in the spin subsystem below  $\lambda$ -point are the nature of the wide array of specific properties demonstrating by the  $^4\text{He}$ .

## REFERENCES

- <sup>1</sup>A. Rybalko, S. Rubets, E. Rudavskii, V. Tikhy, S. Tarapov, R. Golovashchenko, and V. Derkach, *Phys. Rev. B* **76**, 140503 (2007).
- <sup>2</sup>A. Rybalko, S. Rubets, E. Rudavskii, V. Tikhy, V. Derkach, and S. Tarapov, *J. Low Temp. Phys.* **148**, 527 (2007).



- <sup>3</sup>A. S. Rybalko and S. P. Rubets, E. Y. Rudavskii, V. A. Tikhy, R. V. Golovashchenko, V. N. Derkach, and S. I. Tarapov, *Fiz. Nizk. Temp.* **34**, 326 (2008) [*Low Temp. Phys.* **34**, 254 (2008)].
- <sup>4</sup>A. S. Rybalko and S. P. Rubets, E. Y. Rudavskii, V. A. Tikhy, S. I. Tarapov, R. V. Golovashchenko, and V. N. Derkach, *Fiz. Nizk. Temp.* **34**, 631 (2008) [*Low Temp. Phys.* **34**, 497 (2008)].
- <sup>5</sup>A. Rybalko, S. Rubets, E. Rudavskii, V. Tikhiy, Y. Poluectov, R. Golovashchenko, V. Derkach, S. Tarapov, and O. Usatenko, *Fiz. Nizk. Temp.* **35**, 1073 (2009) [*Low Temp. Phys.* **35**, 837 (2009)].
- <sup>6</sup>A. Rybalko, S. Rubets, E. Rudavskii, V. Tikhiy, Y. Poluectov, R. Golovashchenko, V. Derkach, S. Tarapov, and O. Usatenko, *J. Low Temp. Phys.* **158**, 244 (2010).
- <sup>7</sup>K. A. Chishko and A. S. Rybalko, *Fiz. Nizk. Temp.* **45**, 384 (2019) [*Low Temp. Phys.* **45**, 337 (2019)].
- <sup>8</sup>K. A. Chishko and A. S. Rybalko, *J. Low Temp. Phys.* **196**, 21 (2019).
- <sup>9</sup>R. J. Donnelly and P. H. Roberts, *J. Low Temp. Phys.* **27**, 687 (1977).
- <sup>10</sup>K. A. Chishko, *Fiz. Nizk. Temp.* **44**, 1393 (2018) [*Low Temp. Phys.* **44**, 1097 (2018)].
- <sup>11</sup>N. Mott and I. Sneddon, *Wave Mechanics and its Applications* (Clarendon Press, 1948).
- <sup>12</sup>P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
- <sup>13</sup>H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pegamon Press, Oxford, 1971).
- <sup>14</sup>T. N. Antsygina and K. A. Chishko, *Fiz. Nizk. Temp.* **40**, 1035 (2014) [*Low Temp. Phys.* **40**, 807 (2014)].
- <sup>15</sup>J. Hutchinson, M. Baker, and F. Marsiglio, *Eur. J. Phys.* **34**, 111 (2013).
- <sup>16</sup>H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, NY, 1977).
- <sup>17</sup>P. Gomba, *Theorie und Lösungsmethoden des Mehrteilchen-Problems der Wellenmechanik* (Basel, 1950).
- <sup>18</sup>S. Flügge, *Practical Quantum Mechanics II* (Springer, 1971).
- <sup>19</sup>V. A. Fock, *Fundamentals of Quantum Mechanics* (MIR Publishers, Moscow, 1979).
- <sup>20</sup>A. A. Radzig and B. M. Smirnov, *Handbook for Atomic and Molecular Physics* (Atomizdat, Moscow, 1980) [in Russian].
- <sup>21</sup>B. Rosen, in *Spectroscopic Data Relative to Diatomic Molecules* (Pergamon, NY, 1970).
- <sup>22</sup>S. N. Suchard and J. E. Melzer (eds.), "Spectroscopic Data," *Homonuclear Diatomic Molecules* (IFI/Plenum, NY, 1976), Vol. 2.
- <sup>23</sup>H. Margenau, *Rev. Mod. Phys.* **11**, 1 (1939).
- <sup>24</sup>A. Van der Merwe, *Z. Phys.* **196**, 212 (1966).
- <sup>25</sup>A. Van der Merwe, *Z. Phys.* **196**, 322 (1966).
- <sup>26</sup>L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory* (Pergamon Press, 1965).
- <sup>27</sup>D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonski, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
- <sup>28</sup>J. Frenkel, *Einführung in die Wellenmechanik* (Julius Springer, Berlin, 1929).
- <sup>29</sup>S. Huzinaga, *Prog. Theor. Phys.* **17**, 169 (1957).
- <sup>30</sup>M. Sakamoto and E. Ishiguro, *Prog. Theor. Phys.* **15**, 37 (1956).
- <sup>31</sup>N. Linn, *Proc. Phys. Soc. Lond. A* **72**, 201 (1958).
- <sup>32</sup>K. A. Chishko, *J. Low Temp. Phys.* **201**, 90 (2020).
- <sup>33</sup>A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (John Wiley & Sons, NY, 1965).
- <sup>34</sup>F. W. J. Olver, *Asymptotics and Special Functions* (Academic Press, 1974).
- <sup>35</sup>V. G. Manzhelii and Y. A. Freiman, *Physics of Cryocrystals* (AIP Press, NY, 1979).
- <sup>36</sup>I. F. Silvera and J. Walraven, *Sci. Am.* **246**, 56 (1982); I. F. Silvera and J. Walraven, *Usp. Fiz. Nauk* **139**, 701 (1983) [in Russian].
- <sup>37</sup>G. Bertone and D. Hooper, *Rev. Mod. Phys.* **90**, 045002 (2018).
- <sup>38</sup>H. I. Ewen and E. M. Purcell, *Nature* **168**, 356 (1951).
- <sup>39</sup>T. Venumadhav, L. Dai, A. Kaurov, and M. Zalzarriaga, *Phys. Rev. D* **98**, 103513 (2018).
- <sup>40</sup>V. N. Lukash and V. A. Rubakov, *Phys-Usp.* **51**, 301 (2008).
- <sup>41</sup>N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, 1965).
- <sup>42</sup>W. J. Meath and J. O. Hirschfelder, *J. Chem. Phys.* **44**, 3210 (1966).
- <sup>43</sup>F. J. Bermejo, B. Fåk, S. M. Bennington, R. Fernández-Perea, C. Cabrillo, J. Dawidowski, M. T. Fernández-Díaz, and P. Verkerk, *Phys. Rev. B* **60**, 15154 (1999).
- <sup>44</sup>W. E. Keller, *Helium-3 and Helium-4* (Plenum Press, NY, 1969).
- <sup>45</sup>L. W. Shubnikov and A. K. Kikoin, *Nature* **138**(3493), 641 (1936).
- <sup>46</sup>P. Kapitza, *Nature* **141**, 74 (1938).
- <sup>47</sup>R. A. Buckingham, *Planet. Space Sci.* **3**, 205 (1961).
- <sup>48</sup>R. M. Jordan and P. E. Siska, *J. Chem. Phys.* **80**, 5027 (1984).
- <sup>49</sup>B. Brutschy and H. Haberland, *Phys. Rev. A* **19**, 2232 (1979).
- <sup>50</sup>D. R. Yarkony, *J. Chem. Phys.* **90**, 7164 (1989).
- <sup>51</sup>K. K. Sunil, J. Lin, H. Siddiqui, P. E. Siska, and K. D. Jordan, *J. Chem. Phys.* **78**, 6190 (1983).
- <sup>52</sup>D. R. Scott, E. M. Greenwalt, J. C. Browne, and F. A. Matsen, *J. Chem. Phys.* **44**, 2981 (1966).
- <sup>53</sup>E. Fermi, *Z. Phys.* **60**, 320 (1930).
- <sup>54</sup>J. D. Jackson, *Classical Electrodynamics* (John Wiley, NY, 1962).
- <sup>55</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, NY, 1954).
- <sup>56</sup>A. S. Rybalko, *Fiz. Nizk. Temp.* **30**, 1321 (2004) [*Low Temp. Phys.* **30**, 994 (2004)].
- <sup>57</sup>A. S. Rybalko and S. P. Rubets, *Fiz. Nizk. Temp.* **31**, 820 (2005) [*Low Temp. Phys.* **31**, 623 (2005)].
- <sup>58</sup>T. N. Antsygina, M. I. Poltavskaya, and K. A. Chishko, *Phys. Solid State* **44**, 1268 (2002).
- <sup>59</sup>R. K. Pathria, *Statistical Mechanics* (Butterworth & Heinemann, Oxford, 2000).
- <sup>60</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pegamon Press, Oxford, 1958).
- <sup>61</sup>S. Huzinaga, *Prog. Theor. Phys.* **15**, 512 (1956).
- <sup>62</sup>P. Rosen, *J. Chem. Phys.* **18**, 1182 (1950).
- <sup>63</sup>P. Cantini, M. G. Dondi, G. Scoles, and F. Torello, *J. Chem. Phys.* **56**, 1946 (1972).
- <sup>64</sup>J. D. Van der Waals, Over de Continuïteit van den Gas-en Vloeistofoestand (Thesis, Leiden, 1873); J. D. Van der Waals, Nobel Lecture (1910).
- <sup>65</sup>F. London, *Z. Phys.* **63**, 245 (1930).
- <sup>66</sup>L. Tonks, *Phys. Rev.* **50**, 955 (1936).
- <sup>67</sup>L. D. Landau and E. M. Lifshitz, *Classical Field Theory* (Pergamon, NY, 1971).
- <sup>68</sup>S. Herminghaus, *Europhys. Lett.* **42**, 443 (1998).
- <sup>69</sup>M. S. Bryan, *Inelastic Neutron Scattering of Nanoconfined Superfluid Helium* (Indiana University, 2018).
- <sup>70</sup>K. A. Chishko, T. N. Antsygina, and M. I. Poltavskaya, *J. Low Temp. Phys.* **187**, 468 (2017).
- <sup>71</sup>K. A. Chishko, *Fiz. Nizk. Temp.* **44**, 154 (2018) [*Low Temp. Phys.* **44**, 114 (2018)].
- <sup>72</sup>A. R. Verma and P. Krishna, *Polymorphism and Polytypism in Crystals* (Wiley, NY, 1966).
- <sup>73</sup>B. I. Nikolin, Multilayer Structures and Polytypism in Metal Alloys (Naukova Dymka, Kiev, 1984) [in Russian].
- <sup>74</sup>L. D. Landau and E. M. Lifshitz, *Dokl. AN SSSR* **100**, 669 (1955).

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