

Low-energy excitations in helium-like dimer within an exact diagonalization approach

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The non-relativistic quantum-mechanical problem on bound states of four interacting spinless electrons moving in the Coulomb field of two attractive point centers with $Z_0 = 2$ spaced at fixed distance R_0 (${}^4\text{He}_2$ dimer within Born–Oppenheimer–Heitler–London approximation) has been solved rigorously through exact diagonalization (expansion on truncated orthonormalized basis) method. The four-spin-conditioned relativistic corrections (of order $\sim 1/c^2$) to the ground state level of the dimer have been calculated with exact diagonalization on spin cluster, the spectrum and eigenvectors of the spin problem have been obtained. It is shown that pair spin coupling is antiferromagnetic with exchange constant of 12 K (it provides antisymmetry of the spin-singlet ground-state wave function for isolated ${}^4\text{He}$ atom with two fermions coupled within the unitary spatially symmetric shell), but within four-electron shell of ${}^4\text{He}_2$ dimer this fact yields the quintet ground state of the four-spin cluster totally antisymmetric relative to pair permutations. The exchange within the interatomic bond depends on the interatomic distance, so that there is a coupling between spin and phonon degrees of freedom which leads to renormalization of phonon spectrum in condensed phase as compared to the corresponding spinless medium. This effect can be interpreted as a direct analog of translation-rotation interaction in molecular cryocrystals.

Keywords: He–He interatomic interaction, relativistic corrections, spin-spin interaction.

1. Introduction

The most part of modern interpretations for observed properties of liquid and solid helium is based on the postulate that the interatomic interaction in helium is pure van der Waals in its nature. Atom-atom potentials [1] as a basic concept for description of interatomic interaction in gases, liquids and solids is well-known approach to treat physical and chemical properties of different media, but it is not so successful for helium condensed phases.

Specific response of superfluid helium on external electromagnetic exposure have been discovered experimentally over last decade [2–9]. The most characteristic feature of the mentioned experiments is a manifestation of resonant absorption on a certain temperature-dependent low-frequency mode (of 150–180 GHz) which behaves like specific eigenstate of superfluid phase in ${}^4\text{He}$ below λ -point [4,8,9]. The nature of this phenomenon is still not quite understood, but it is evident that the corresponding effects can not be interpreted properly without correct solution of the quantum mechanical problem for a helium atom interacting with array of neighboring helium atoms. It should be pointed clearly the intra-atomic degrees of freedom responsible for the resonant effects in helium condensed phases.

In this paper we present the formally exact solution for the non-relativistic quantum mechanical problem of helium-helium interaction treated within Born–Oppenheimer–Heitler–London approach [10,11] (four spinless electrons moving in the Coulomb field of two nuclei with $Z_0 = 2$ spaced at fixed distance R_0) improved with spin-conditioned relativistic corrections of order $1/c^2$. The one-parametric spectrum $\mathcal{E}_n(R_0)$ of bound states for the problem has been obtained with exact diagonalization procedure [12,13] at arbitrary values of R_0 (Sec. 4). We are interested in low-temperature properties of condensed helium phases, so that we keep only the spatial ground state of the system. Then we include spin-conditioned relativistic corrections of order $1/c^2$ (spin-orbit and spin-spin coupling). It is found that due to symmetry of the ground-state wave function the matrix elements of spin-orbit coupling (linear in spin operators) vanish, but spin-spin coupling (bilinear in spin operators) gives a spin density matrix which describes a four-spin cluster within internuclear bond with mutual antiferromagnetic pair exchange of order 12 K. The spectrum and eigenvectors of the spin density matrix have been obtained through exact Jacobi diagonalization of 16×16 matrix of integer elements. The ground

state of the spin problem is triplet with eigenvectors antisymmetric relative to the odd number of pair permutations, in this sense it is compatible with the parity of the spatial ground state within the complete wave function of the system. The results are discussed in Sec. 6.

2. Two interacting helium atoms (helium dimer)

Below we use the Hartree atomic system of units with electronic mass $m_e = 1$ and spatial scale normalized on the Bohr radius $a_0 = \hbar^2 / m_e e^2$. The physical system under study consists of six charged particles, namely, two nuclei with the positive charges $Z_1 = Z_2 = Z_0 = +2$ and four electrons which we denote as ‘‘a’’, ‘‘b’’, ‘‘c’’ and ‘‘d’’ particles with charges $Z_a = Z_b = Z_c = Z_d = -1$. We suppose the coordinate origin is coincide with one of the nucleus, so that the radius-vector of the second one is \mathbf{R}_0 , and coordinates of the electrons are \mathbf{r}_a , \mathbf{r}_b , \mathbf{r}_c and \mathbf{r}_d , respectively. Thus, the Hamiltonian of the problem takes the form

$$\hat{H}_0(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = -\frac{1}{2\mu} \Delta^{(\text{nuc})}(\mathbf{R}_0) + \frac{Z_1 Z_2}{R_0} + H^{(e)}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) + H_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d, \mathbf{R}_0), \quad (1)$$

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

$$\hat{H}^{(e)}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) = -\sum_s \left[\frac{1}{2} \Delta^{(e)}(\mathbf{r}_s) + \frac{Z_1}{r_s} \right] + \frac{1}{2} \sum_{s \neq s'} \frac{1}{|\mathbf{r}_s - \mathbf{r}_{s'}|} \quad (s, s' = a, b, c, d), \quad (2)$$

and H_{int} describes the attraction between electrons and the second nucleus,

$$\hat{H}_{\text{int}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = -Z_2 \sum_s \frac{1}{|\mathbf{r}_s - \mathbf{R}_0|} \leq 0. \quad (3)$$

The Hamiltonian (1) describes an exact non-relativistic dynamics of the system, including internuclear motion. To take into account the dynamics of heavy repulsive nucleus we have to use a basis incorporate the functions of continuous spectrum, whereas the electronic part of the problem should be based on functions of discrete spectrum [12]. However, if we are interested in some specific applications of the problem restricted to interatomic interactions in condensed helium matter then the interatomic distance \mathbf{R}_0 has a rather narrow range of variation, and the system can be treated on the qualitative level within Heitler–London approximation (HLA) [10]. The HLA Hamiltonian can be obtained from Eq. (1) in the limit $\mu \rightarrow \infty$.

3. Eigenstates of four-electron two-center system

The Schrödinger equation with Hamiltonian (1) within HLA,

$$\hat{H}_0 \Psi(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = \mathcal{E} \Psi(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0), \quad (4)$$

is the linear differential equation of second order in partials depending on eleven spatial variables $\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d$ and one free parameter \mathbf{R}_0 . The procedure of exact diagonalization is described in Ref. 12 for isolated ^4He atom (two electrons in a central field). The problem studied in the present paper is more complicated despite the principal analogy with treatment of Ref. 12. The complication is due to essentially wider basis which is necessary for the procedure, and the presence of ‘external’ field (3) from the second nucleus.

We consider only bound states of four-particle Hamiltonian (1) with discrete spectrum $\mathcal{E} < 0$. The exact solution $\Psi(\mathbf{r}_a, \mathbf{r}_b)$ of the linear partial differential equation (4) can be written as an expansion [14]

$$\Psi(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = \sum_{p=1}^{\infty} c_p(\mathbf{R}_0) u_p(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) \quad (5)$$

over a complete set $\{u_p(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d)\}$ of functions orthonormalized with standard condition

$$\langle u_p | u_q \rangle = \int \prod_s d^3 \mathbf{r}_s u_p^+ u_q = \delta_{pq}, \quad (6)$$

where $s = a, b, c, d$, and δ_{pq} is Kronecker delta.

We select the basis $\{u_p(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d)\}$ as every possible direct products,

$$u_p(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) \equiv \left\langle \begin{array}{ccc} n_a & l_a & m_a \\ n_b & l_b & m_b \\ n_c & l_c & m_c \\ n_d & l_d & m_d \end{array} \right\rangle = \prod_s \psi_{n_s l_s m_s}(\alpha r_s, \vartheta_s, \varphi_s) \quad (7)$$

of single-particle hydrogen-like functions [15–17],

$$\psi_{nlm}(\alpha r) = \mathcal{R}_{nl}(\alpha r) Y_{lm}(\vartheta, \varphi) \equiv |nlm\rangle, \quad (8)$$

where $Y_{lm}(\vartheta, \varphi)$ are spherical harmonics in standard determination [17,18], and radial function $\mathcal{R}_{nl}(\alpha r)$ depends on radial coordinate renormalized by scale parameter [12] $\alpha > 0$, and radial function is

$$\mathcal{R}_{nl}(\alpha r) = -\frac{2\alpha^{3/2}}{n^2 \sqrt{(n-l-1)! \sqrt{(n+l)!}}} \times \left(\frac{2\alpha r}{n} \right)^l \exp\left(-\frac{\alpha r}{n}\right) L_{n-l-1}^{(2l+1)}\left(\frac{2\alpha r}{n}\right), \quad (9)$$

where $L_n^{(\lambda)}(x)$ are Laguerre polynomials [42]

$$L_p^{(\lambda)}(x) = p!(\lambda + p)! \sum_{k=0}^p \frac{(-x)^k}{k!(p-k)!(\lambda+k)!}. \quad (10)$$

With respect to Eq. (10) the radial functions $\mathcal{R}_{nl}(\alpha r)$ can be represented in the explicit form,

$$\begin{aligned} \mathcal{R}_{nl}(\alpha r) = & -\frac{2\alpha^{3/2}}{n^2} \sqrt{(n-l-1)!} \sqrt{(n+l)!} \left(\frac{2\alpha r}{n}\right)^l \times \\ & \times \exp\left(-\frac{\alpha r}{n}\right) \sum_{k=0}^p \frac{(-1)^k}{k!} \frac{\left(\frac{2\alpha r}{n}\right)^k}{(n-l-k-1)!(2l+k+1)!}. \end{aligned} \quad (11)$$

Note, that functions \mathcal{R}_{nl} of the set Eq. (9) are orthonormalized at any real positive $\alpha > 0$ [17]. The case $\alpha = 1$ in single-particle function corresponds to the simple hydrogen atom. For two-electron helium shell we have $\alpha = Z_0 - \sigma$, where $0 < \sigma < 1$ is the screening parameter [12,18,19].

Each basis function number

$$p \rightarrow \left\{ \begin{matrix} n_a & l_a & m_a \\ n_b & l_b & m_b \\ n_c & l_c & m_c \\ n_d & l_d & m_d \end{matrix} \right\} \quad (12)$$

is determined in univocal correspondence to a complete set of single-particle hydrogen-like quantum numbers. The complete basis must include all functions $u_{n_a l_a m_a}(\mathbf{r}_a)$, $u_{n_b l_b m_b}(\mathbf{r}_b)$, $u_{n_c l_c m_c}(\mathbf{r}_c)$ and $u_{n_d l_d m_d}(\mathbf{r}_d)$ corresponding to all degenerate states with different m_a, m_b, m_c and m_d at given $n_a, n_b, n_c, n_d, l_a, l_b, l_c, l_d$. If vector $\mathbf{R}_0 = R_0(0,0,1)$ is oriented along z axis, then the projection L_z of the total angular momentum of the system is the integral of motion, and eigenvalues M of the operator \hat{L}_z are

$$M = m_a + m_b + m_c + m_d = 0, \pm 1, \pm 2, \dots \quad (13)$$

These values are good quantum numbers of the general problem. It means that every pure eigenstate of the Hamiltonian (1) can be represent as infinite superposition of direct compositions of single-particle wave functions with arbitrary m_a, m_b, m_c, m_d , but only under condition (13). This property will be used below for classification of the electronic states.

As a result, we will find the solution of the problem

$$\sum_{q=1}^{\infty} [H_{pq}(R_0) - \mathcal{E}(R_0)\delta_{pq}] c_q(\mathbf{R}_0) = 0, \quad (14)$$

with the basis (7). Matrix elements are (cmp. Ref. 12)

$$\begin{aligned} H_{pq}(R_0) = \langle u_p | H | u_q \rangle = & -\frac{\alpha^2}{2} \left(\frac{1}{n_a^2} + \frac{1}{n_b^2} + \frac{1}{n_c^2} + \frac{1}{n_d^2} \right) \delta_{pq} - \sigma \sum_s \left\langle \begin{matrix} n_{a_1} & l_{a_1} & m_{a_1} \\ n_{b_1} & l_{b_1} & m_{b_1} \\ n_{c_1} & l_{c_1} & m_{c_1} \\ n_{d_1} & l_{d_1} & m_{d_1} \end{matrix} \middle| \frac{1}{r_s} \middle| \begin{matrix} n_{a_2} & l_{a_2} & m_{a_2} \\ n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \right\rangle - \\ & -Z_2 \sum_s \left\langle \begin{matrix} n_{a_1} & l_{a_1} & m_{a_1} \\ n_{b_1} & l_{b_1} & m_{b_1} \\ n_{c_1} & l_{c_1} & m_{c_1} \\ n_{d_1} & l_{d_1} & m_{d_1} \end{matrix} \middle| \frac{1}{|\mathbf{r}_s - \mathbf{R}_0|} \middle| \begin{matrix} n_{a_2} & l_{a_2} & m_{a_2} \\ n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \right\rangle + \frac{1}{2} \sum_{s \neq s'} \left\langle \begin{matrix} n_{a_1} & l_{a_1} & m_{a_1} \\ n_{b_1} & l_{b_1} & m_{b_1} \\ n_{c_1} & l_{c_1} & m_{c_1} \\ n_{d_1} & l_{d_1} & m_{d_1} \end{matrix} \middle| \frac{1}{|\mathbf{r}_s - \mathbf{r}_{s'}|} \middle| \begin{matrix} n_{a_2} & l_{a_2} & m_{a_2} \\ n_{b_2} & l_{b_2} & m_{b_2} \\ n_{c_2} & l_{c_2} & m_{c_2} \\ n_{d_2} & l_{d_2} & m_{d_2} \end{matrix} \right\rangle, \end{aligned} \quad (15)$$

where $s, s' = a, b, c, d$ and $\sigma = Z_1 - \alpha$ is the screening parameter [12]. Below, for simplicity, we neglect the screening ($\sigma = 0$), so that $\alpha = Z_1$. All the matrix elements had been calculated in Ref. 12, except of the last term in Eq. (15) which is a sum of expressions

$$\begin{aligned} & \langle n_1 l_1 m_1 || r - \mathbf{R}_0 |^{-1} | n_2 l_2 m_2 \rangle = \\ & = \sum_{|l_1 - l_2|}^{l_1 + l_2} \mathcal{I}_l \left(\begin{matrix} n_1 & l_1 \\ n_2 & l_2 \end{matrix} \middle| \alpha R_0 \right) W_l \left(\begin{matrix} l_1 & m_1 \\ l_2 & m_2 \end{matrix} \middle| \Theta, \Phi \right), \end{aligned} \quad (16)$$

where Θ and Φ are polar and azimuthal angles of the vector \mathbf{R}_0 , and

$$\mathbf{R}_0 = R_0(\sin \Theta \cos \Phi, \sin \Theta \sin \Phi, \cos \Theta).$$

At chosen orientation of the \mathbf{R}_0 along z axis we have $\Theta = 0$, so that Φ can be an arbitrary value within interval $[0, 2\pi)$, say $\Phi = 0$. As a result,

$$\begin{aligned} W_l \left(\begin{matrix} l_1 & m_1 \\ l_2 & m_2 \end{matrix} \middle| 0, 0 \right) = & \sqrt{(2l_1 + 1)(2l_2 + 1)} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \times \\ & \times \sum_{m=-l}^l (-1)^{m+m_1} \begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_2 & -m \end{pmatrix}, \end{aligned} \quad (17)$$

where $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ are Wigner $3j$ -symbols [20]. Function \mathcal{I}_l as integral over radial variables has the form (cmp. Ref. 12)

$$\mathcal{I}_l \left(\begin{matrix} n_1, & l_1 \\ n_2, & l_2 \end{matrix} \middle| \alpha R_0 \right) = \frac{4\alpha}{n_1^2 n_2^2} \frac{\sqrt{\tau_1! \tau_2! \nu_1! \nu_2!}}{a^{l_1+l_2+2}} \left(\frac{2}{n_1} \right)^{l_1} \left(\frac{2}{n_2} \right)^{l_2} \times \sum_{k_1=0}^{\tau_1} \sum_{k_2=0}^{\tau_2} \frac{(-1)^{k_1+k_2}}{a^{k_1+k_2} k_1! k_2! (\lambda_1+k_1)! (\lambda_2+k_2)! (\tau_1-k_1)! (\tau_2-k_2)!} \times \left(\frac{2}{n_1} \right)^{k_1} \left(\frac{2}{n_2} \right)^{k_2} \times \left\{ \frac{(l+N)!}{(\alpha\alpha R_0)^{l+1}} \left[1 - \exp(-\alpha\alpha R_0) \sum_{k=0}^{l+N} \frac{(\alpha\alpha R_0)^k}{k!} \right] + (\alpha\alpha R_0)^l (N-l-1)! \exp(-\alpha\alpha R_0) \sum_{k=0}^{N-l-1} \frac{(\alpha\alpha R_0)^k}{k!} \right\}. \quad (18)$$

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

All terms in Eq. (15) are matrix elements of pair interactions because the Hamiltonian (1) describes only pair interactions between non-polarized elementary particles (electrons and protons) belonging to the interacting helium atoms. The polarizability is only property of integrated atom built of charges with different signs.

4. The spectrum of the problem

In the present statement the problem under study is rather close to well-known problem of many-electron diatomic molecule [16]. The standard approach [16] to this problem is based on postulate of electron motion within a certain self-consistent field (SCF) which ignores some details of individual electronic state, but the corresponding features can be described properly using exact diagonalization scheme. In this connection we will not classify here the electronic states with standard shell notations, referring only to conservation law for z -projection of the total angular momentum.

We use the basis (7) [12] built as direct composition of four five-component single-particle bases (8) with $n \leq 2$ $l \leq 1$, namely,

$$\{|100\rangle, |200\rangle, |210\rangle, |21-1\rangle, |211\rangle\}.$$

As a result, we obtain the total basis of $5^4 = 625$ functions. However, before start of the main calculations we make some remarks about numerical procedure using more simpler example of hydrogen dimer (two attractive Coulomb centers with $Z_1 = Z_2 = 1$ and two interacting electrons).

4.1. Hydrogen–hydrogen bond

To be sure that our procedure works in a proper way, we calculate the problem of two electrons at two nucleus (H–H dimer). The results are presented on Fig. 1, and they are closely related to well-known Morse curves obtained with the simplest variational procedure [10]. It is essential for our procedure that there is an optimal dimension of the basis which gives the minimal value of the calculated energy. It can be shown from Fig. 1(a) that the curve obtained with basis of $N = 25$ is much lower than one calcu-

lated with basis of $N = 155$, and this last curve runs closely to the curve obtained with $N = 4$. Thus, the basis of $N = 25$ should be considered as an optimal case.

Another fact is a proof of the limit $R_0 \rightarrow 0$ where after omitting the repulsive term $1/R_0$ we have to get the spectrum of two-electron helium atom [12]. As it seen from Fig. 1(b), the energy spectrum of H–H in the limit $R_0 \rightarrow 0$ is of 15% higher than the exact helium spectrum [12], but it is more essential for our goals that it is only numerical discrepancy, and the structure of helium spectrum remains unchanged. It means that we can trust our calculation procedure at finite R_0 .

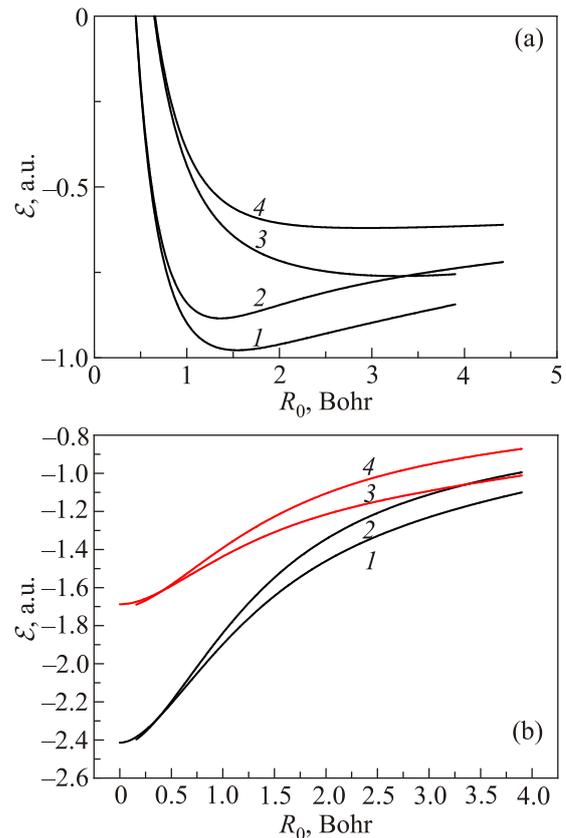


Fig. 1. Two lowest states (symmetric and antisymmetric) of H–H dimer as a function of internuclear distance R_0 (a). Plot (b) shows the run of the Morse curves without of $1/R_0$ repulsion, and the curves tend at $R_0 \rightarrow 0$ to the values adequate to corresponding energy levels of simple helium atom [12]. Curves 1, 3 corresponded to basis with 25 functions, and curves 2, 4 corresponded to basis with 155 functions.

4.2. Helium–helium bond

The total representation is reducible and splits onto irreducible representations corresponding to determined value of $M = m_a + m_b + m_c + m_d$ (the projection \hat{L}_z of the total angular momentum of the system on \mathbf{R}_0 direction is an integral of motion). However, due to only pair interaction between particles in the Hamiltonian (1) (see Eqs. (2), (3)) for each matrix element of Eq. (15) exists the condition $m_{s_1} + m_{s_2} \leq l_{s_1} + l_{s_2} \leq 2$ which means that there are no reason taking into account the elements with $M > 2$, despite formally such cases are acceptable. Thus, the basis is shortened up to 599 elements (195 elements of $M = 0$, 288 = 2·144 elements of $M = \pm 1$, and 116 = 2·58 elements of $M = \pm 2$).

After diagonalization according to the procedure described in Ref. 12 we have spectrum $\mathcal{E}_j(R_0)$ and eigenvectors with components $e_p^{(j)}(E_0)$. Three lowest levels of the

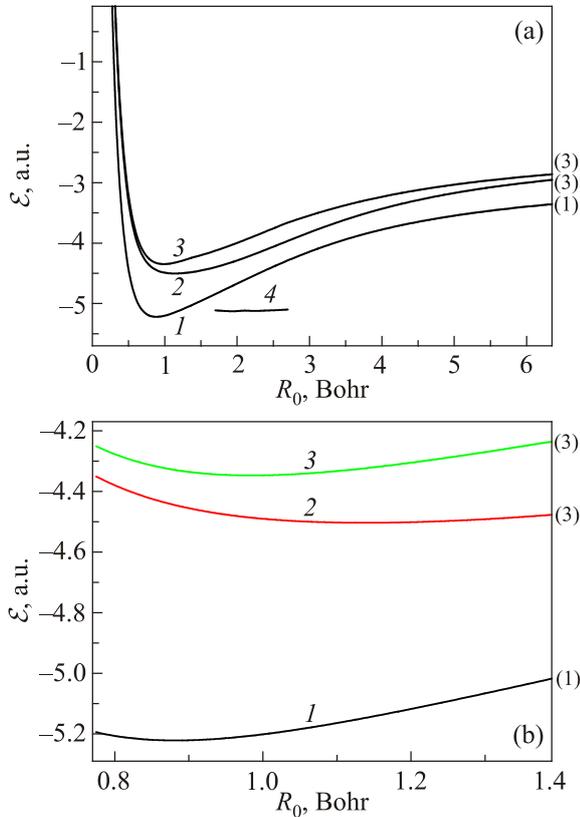


Fig. 2. Three lowest states (Morse curves 1–3) of ${}^4\text{He}-{}^4\text{He}$ dimer as function of internuclear distance R_0 (a). For comparison, curve 4 on Fig. 2(a) is the variational calculation from Ref. 21. Plot (b) shows the run of the Morse curves in the vicinity of their minima. The numbers in brackets on right margins indicate the degeneracy of the corresponding level. The distances and energies corresponding to the minima of the curves are summarized in Table 1. The plotted functions are presented in atomic units.

spectrum as functions of R_0 (Morse curves [11]) are shown on Figs. 2(a), (b). Each of the branches of the spectrum corresponding to the bound states ($\mathcal{E} < 0$) has a minimum $\mathcal{E}_{j \min}$ at its own characteristic distance $R_{j \min}$. All the data are accumulated in the Table 1.

Table 1. Extremal parameters of low-lying levels for ${}^4\text{He}-{}^4\text{He}$ dimer

| Level | $R_{j \min}$ | | $\mathcal{E}_{j \min}$ | | Deg. |
|-------|--------------|---------|------------------------|----------|------|
| | Bohr | Å | a.u. | eV | |
| 1 | 0.88125 | 0.46618 | -5.22163 | -142.081 | (1) |
| 2 | 1.13875 | 0.60240 | -4.50354 | -122.541 | (3) |
| 3 | 0.98375 | 0.52040 | -4.34744 | -118.294 | (3) |

As we can see from Fig. 2(a), the slope of the Morse curves is rather slower than expected from the van der Waals prediction $\sim 1/R_0^6$. This fact is caused by pair correlation between electrons (due to $|\mathbf{r}_s - \mathbf{r}_{s'}|^{-1}$ in the Hamiltonian (1)) which in reality can not be neglected at $R_0 \rightarrow \infty$ because all the distances $|\mathbf{r}_s - \mathbf{r}_{s'}|$ contribute in the matrix elements of Eq. (15). It is consequence of the instantaneous correlation between particle positions in non-relativistic Schrödinger quantum mechanics. To avoid the corresponding faults the finite speed of the signal propagation between interacting particles should be taken into account [22], but the necessary corrections becomes essential only if $R_0 > 2-3$. On the other hand, at $R_0 \rightarrow 0$ the calculation procedure developed in the present work gives bound states with $\mathcal{E}_j(R_0) > 0$, whereas, in fact, the states with positive energy must correspond to infinite motion of the particles (dissociation of the ${}^4\text{He}-{}^4\text{He}$ dimer). To describe properly the states with positive energy we have to include in the completed basis set the wave function of the continuous spectrum and take into account the omitted first term in the Hamiltonian (1). However, in view of the declared goals of the present paper, there are no reason to consider the both mentioned circumstances. We are only interested in the lowest energy levels of the system in the narrow vicinity of $R_{j \min} \sim 1$ because just this case corresponds to the atomic configuration typical for condensed (liquid and solid) helium phases.

5. Relativistic corrections to the ground state of the helium dimer

All the relativistic corrections to the helium atom were discussed in details by Bethe [22]. There are only two of them (spin-orbit and spin-spin coupling) which lead to the splitting of the helium atomic levels. Spin-orbit coupling has the Hamiltonian (cmp. with H_3 in Eq. (39.14) of the book Ref. 22)

$$\begin{aligned} \hat{H}_{so}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = & \frac{Z_0 g_s \alpha_s^2}{4} \left\{ \sum_s \hat{\sigma}_s \left[\frac{\mathbf{r}_s}{r_s^3} \times -i\nabla_s \right] + \right. \\ & \left. + \sum_s \hat{\sigma}_s \left[\frac{\mathbf{r}_s - \mathbf{R}_0}{|\mathbf{r}_s - \mathbf{R}_0|^3} \times -i\nabla_s \right] - \right. \\ & \left. - \frac{1}{Z_0} \sum_s \hat{\sigma}_s \sum_{s' \neq s} \left[\frac{\mathbf{r}_s - \mathbf{r}_{s'}}{|\mathbf{r}_s - \mathbf{r}_{s'}|^3} \times -i(\nabla_s - \nabla_{s'}) \right] \right\}, \quad (19) \end{aligned}$$

where $\alpha_s = 1/137.039$ is Sommerfeld constant, $g_s = 1.001145$ is spin g -factor, and $\hat{\sigma}$ 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 [19,23,24] 1/2 has been taken into account in Eq. (19) as well.

The next correction of our interest is Hamiltonian for pair interaction between magnetic moments of individual electrons (cmp. with H_5 in Eq. (39.14) of the Ref. [22],

$$\begin{aligned} \hat{H}_{ss}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) = & \frac{g_s^2 \alpha_s^2}{4} \left\{ \frac{8\pi}{3} \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'} \delta(\mathbf{r}_s - \mathbf{r}_{s'}) + \right. \\ & \left. + \sum_{s \neq s'} \frac{1}{|\mathbf{r}_s - \mathbf{r}_{s'}|^3} \left[\hat{\sigma}_s \hat{\sigma}_{s'} - 3 \frac{((\mathbf{r}_s - \mathbf{r}_{s'}) \hat{\sigma}_s)((\mathbf{r}_s - \mathbf{r}_{s'}) \hat{\sigma}_{s'})}{|\mathbf{r}_s - \mathbf{r}_{s'}|^2} \right] \right\} \quad (20) \end{aligned}$$

(nuclear spin of the ^4He atom is equal to zero). The $\sim \delta(\mathbf{r}_s - \mathbf{r}_{s'})$ -like term in the first sum within curly brackets of Eq. (20) had been discussed by Landau and Berestetskii [25] in 1949 when studying the interactions between electron-positron pair (1/2-spin particles with opposite charges), and then it was applied to derive some relativistic correction for two-electron helium atom [26–28]. This problem was discussed in the Bethe book [22]. It should be noted that the goal of Ref. [25] was to describe an interaction between magnetic moments of electron-positron pair, $\hat{\mu}_p = (e\hbar/2m_p c) \hat{\sigma}_p$ and $\hat{\mu}_e = -(e\hbar/2m_e c) \hat{\sigma}_e$, respectively. Thus, for electron-electron pair should be described with expression (20) of opposite sign. This fact was overlooked by authors of Refs. [22, 26–28]. Here we are trying to make up for the deficiency in this problem. Only at positive pair spin exchange the ground state of simple helium atom (two electrons within the unitary shell) is the singlet antisymmetric relative to spins permutation. It will be shown below that only positive spin-spin ex-

change leads to correct parity of the spin wave function within the ground state of $^4\text{He}_2$ dimer (four spins with pair exchange interaction or four-spin Heisenberg cluster). The second sum in curly brackets of Eq. (20) is a set of direct static pair interactions between intrinsic magnetic moments of electrons [29].

The completed Hamiltonian of the system (Eq. (1) with corrections Eqs. (19), (20)) has to be averaged over spatial ground state $\Psi_1(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0)$ of the helium dimer with energy $\mathcal{E}_1(R_0)$ shown in Fig. 1 (see Seq. 4). As a result, we have

$$\begin{aligned} \rho(\hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c, \hat{\sigma}_d | R_0) = & \langle \Psi_1 | \hat{H}_0 + \hat{H}_{so}^{\hat{\sigma}} + \hat{H}_{ss}^{\hat{\sigma}} | \Psi_1 \rangle = \\ = & \mathcal{E}_1(R_0) + A_{so}(R_0) \sum_s \hat{\sigma}_s + A_{ss}(R_0) \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'}. \quad (21) \end{aligned}$$

Thus, the operator in the right side of the Eq. (21) is a spin density matrix which depends only on the spin variables of the four electrons bounded in the dimer. It describes both spin-orbital coupling (linear in spin operators $\hat{\sigma}_s$) and spin-spin interactions (bilinear in spin operator pairs $\hat{\sigma}_s \hat{\sigma}_{s'}$, $s \neq s'$).

5.1. Spin-orbit coupling

Here we re-write the spin-orbital Hamiltonian (19) in the equivalent form

$$\begin{aligned} \hat{H}_{so}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0) = & \frac{Z_0 g_s \alpha_s^2}{4} \left\{ \sum_s \frac{(\hat{\mathbf{l}}_s \hat{\sigma}_s)}{r_s^3} + \right. \\ & \left. + \sum_s \frac{(\hat{\mathbf{l}}_s \hat{\sigma}_s)}{|\mathbf{r}_s - \mathbf{R}_0|^3} - \sum_s \frac{[(\mathbf{R}_0 \times -i\nabla_s] \hat{\sigma}_s}{|\mathbf{r}_s - \mathbf{R}_0|^3} - \right. \\ & \left. - \frac{1}{Z_0} \sum_s \hat{\sigma}_s \sum_{s' \neq s} \frac{\hat{\mathbf{l}}_s + \hat{\mathbf{l}}_{s'} - [\mathbf{r}_s, -i\nabla_{s'}] - [\mathbf{r}_{s'}, -i\nabla_s]}{|\mathbf{r}_s - \mathbf{r}_{s'}|^3} \right\}, \quad (22) \end{aligned}$$

where $\hat{\mathbf{l}}_s = [\mathbf{r}_s \times -i\nabla_s]$ is the angular momentum of an electron. It is seen that due to specific symmetry of the wave function $\Psi_1(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0)$ the matrix element $\langle \Psi_1 | \hat{H}_{so}^{\hat{\sigma}} | \Psi_1 \rangle = 0$, so that the spin-orbital coupling does not contribute to the ground-state energy of the He–He dimer. It makes us possible to present the wave function of the ground state as direct product of independent spatial and spin factors.

5.2. Spin-spin interaction

Now we re-write the spin-spin Hamiltonian (20) in the form

$$\begin{aligned} \hat{H}_{ss}^{\hat{\sigma}}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) = & \frac{g_s^2 \alpha_s^2}{4} \left\{ \frac{4\pi}{3} \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'} \delta(\mathbf{r}_s - \mathbf{r}_{s'}) + \frac{1}{2} \sum_{s \neq s'} \frac{(\hat{\sigma}_s)_i (\hat{\sigma}_{s'})_k}{|\mathbf{r}_s - \mathbf{r}_{s'}|^3} \right\} \times \\ & \times \left[\delta_{ik} - 3 \frac{(x_s)_i (x_s)_k + (x_{s'})_i (x_{s'})_k - (x_{s'})_i (x_s)_k - (x_s)_i (x_{s'})_k}{|\mathbf{r}_s - \mathbf{r}_{s'}|^2} \right], \quad (23) \end{aligned}$$

where $i, k = x, y, z$, and δ_{ik} is Kronecker delta, the standard rule for tensor indexes summation is applied. Due to symmetry of the spatial ground-state wave func-

tion, the matrix element of the second sum in Eq. (23) vanishes, and finally we have matrix element of the spin-spin Hamiltonian

$$\langle \Psi_1 | \hat{H}_{ss}(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d) | \Psi_1 \rangle = \frac{\pi}{3} g_s^2 \alpha_s^2 \sum_{s \neq s'} \langle \Psi_1(R_0) | \left(\delta(\mathbf{r}_s - \mathbf{r}_{s'}) + \frac{3}{8\pi |\mathbf{r}_s - \mathbf{r}_{s'}|^3} \right) | \Psi_1(R_0) \rangle \hat{\sigma}_s \hat{\sigma}_{s'}. \quad (24)$$

Taken into account that $\langle |\mathbf{r}_s - \mathbf{r}_{s'}|^{-3} \rangle \sim 1/8$ we can neglect the second term in braces of Eq. (24), and

$$\begin{aligned} \rho(\hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c, \hat{\sigma}_d | R_0) &= \\ &= \mathcal{E}_1(R_0) + \frac{\pi}{3} g_s^2 \alpha_s^2 F(R_0) \sum_{s \neq s'} \hat{\sigma}_s \hat{\sigma}_{s'}, \end{aligned} \quad (25)$$

where

$$F(R_0) = \int d^3 \mathbf{r}_s d^3 \mathbf{r}_{s'} \delta(\mathbf{r}_s - \mathbf{r}_{s'}) [\Psi_1(\mathbf{r}_a, \mathbf{r}_b, \mathbf{r}_c, \mathbf{r}_d | \mathbf{R}_0)]^2 \quad (26)$$

in view of Ψ_1 is real function, symmetric over all pairs of the spatial variables. The function $F(R_0)$ is plotted on Fig. 3.

Hamiltonian (25) is a formal analog of antiferromagnetic Heisenberg model [30] applied to four-electron cluster within an integrated He dimer,

$$\begin{aligned} \rho(\hat{\sigma}_a, \hat{\sigma}_b, \hat{\sigma}_c, \hat{\sigma}_d | R_0) - \mathcal{E}_1(R_0) &= \\ &= J(R_0) (\hat{\sigma}_a \hat{\sigma}_b + \hat{\sigma}_a \hat{\sigma}_c + \hat{\sigma}_a \hat{\sigma}_d + \hat{\sigma}_b \hat{\sigma}_c + \hat{\sigma}_b \hat{\sigma}_d + \hat{\sigma}_c \hat{\sigma}_d), \end{aligned} \quad (27)$$

where

$$\begin{aligned} J(R_0) &= \frac{2\pi}{3} g_s^2 \alpha_s^2 F(R_{0\min}) = 3.8 \cdot 10^{-5} = \\ &= 1.656598 \cdot 10^{-15} \text{ erg} = 12 \text{ K} \end{aligned} \quad (28)$$

is exchange constant. Hamiltonian (27) can be easily prepared with exact diagonalization procedure. Let us use the 16-component basis

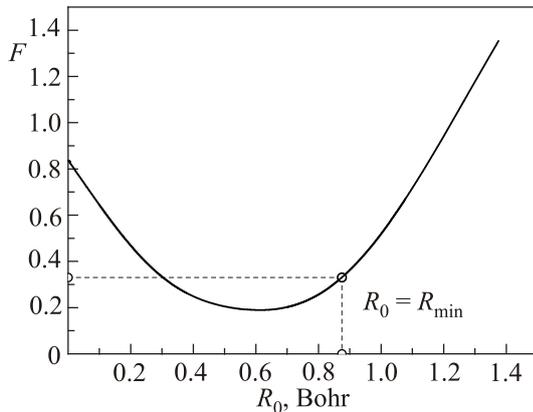


Fig. 3. Exchange coefficient of the spin subsystem of $^4\text{He}-^4\text{He}$ dimer as function of internuclear distance R_0 . The point $R_{0\min}$ on the graph corresponds to the minimum of potential Morse curve of the ground state on Fig. 2.

$$\begin{pmatrix} \alpha(a) \\ \beta(a) \end{pmatrix} \otimes \begin{pmatrix} \alpha(b) \\ \beta(b) \end{pmatrix} \otimes \begin{pmatrix} \alpha(c) \\ \beta(c) \end{pmatrix} \otimes \begin{pmatrix} \alpha(d) \\ \beta(d) \end{pmatrix}, \quad (29)$$

where

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

are one-spin basis vectors. The Hermitian 16×16 matrix of integer elements has been diagonalized with standard Jacobi procedure. The ground state of the spin cluster is quintet with energy $\mathcal{E}_s^{(0)} = -2J(R_0) = -24 \text{ K}$ (it is of about 0.1% of the ground-state energy of spinless dimer), and each of five eigenvectors of the ground state changes its sign only after odd number of pair permutations within basis composition (29), so that the spin ground state has the parity compatible with Pauli principle for the complete ground state of dimer. The most essential fact is degeneracy of the ground state. The quintet ground state can be splitted through some external interaction, for example, through coupling between spin subsystem and lattice phonons because the exchange constant $J(R_0)$ of the spin subsystem is an explicit function of the internuclear distance R_0 .

Let us use the simplest lattice model of monoatomic condensed phase (liquid or solid [31]) where the number of sites coincides with the number of atoms in the system. There is two spins ($\hat{\sigma}_a^{\mathbf{f}}$ and $\hat{\sigma}_b^{\mathbf{f}}$) belong to each site with coordinate \mathbf{f} , and as a result,

$$\begin{aligned} \hat{H}_{ss} &= \frac{J(R_0)}{2} \sum_{\mathbf{f}, \delta} \left[\hat{\sigma}_a^{\mathbf{f}} \hat{\sigma}_a^{\mathbf{f}+R_0\delta} + \right. \\ &\left. + \hat{\sigma}_a^{\mathbf{f}} \hat{\sigma}_b^{\mathbf{f}+R_0\delta} + \hat{\sigma}_b^{\mathbf{f}} \hat{\sigma}_a^{\mathbf{f}+R_0\delta} + \hat{\sigma}_b^{\mathbf{f}} \hat{\sigma}_b^{\mathbf{f}+R_0\delta} \right], \end{aligned} \quad (30)$$

where δ is a unit vector directed to the corresponding nearest neighbor from the first coordination sphere of 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. This scheme means mutual spin-spin interaction between neighboring sites, each interatomic bond is the above-described dimer.

If the lattice contains phonon excitations, then the lattice sites \mathbf{f} and $\mathbf{f} + R_0\delta$ have displacements $\mathbf{u}_{\mathbf{f}}$ and $\mathbf{u}_{\mathbf{f},\delta}$, respectively. As a result, the distance between the sites becomes equal to $|R_0\delta + (\mathbf{u}_{\mathbf{f}\delta} - \mathbf{u}_{\mathbf{f}})|$, and the Hamiltonian (30) takes an additional term

$$\hat{H}_{ss} \rightarrow \hat{H}_{ss} + \hat{H}_{\text{sph}}, \quad (31)$$

where \hat{H}_{sph} describes spin-phonon interaction,

$$\hat{H}_{\text{sph}} = \frac{\partial J(R_0)}{\partial R_0} \sum_{\mathbf{f}, \delta} [(\mathbf{u}_{\mathbf{f}, \delta} - \mathbf{u}_{\mathbf{f}}) \delta] \times \left[\hat{\sigma}_a^{\mathbf{f}} \hat{\sigma}_a^{\mathbf{f}, \delta} + \hat{\sigma}_a^{\mathbf{f}} \hat{\sigma}_b^{\mathbf{f}, \delta} + \hat{\sigma}_b^{\mathbf{f}} \hat{\sigma}_a^{\mathbf{f}, \delta} + \hat{\sigma}_b^{\mathbf{f}} \hat{\sigma}_b^{\mathbf{f}, \delta} \right], \quad (32)$$

with positive derivative $\partial J(R_0)/\partial R_0 > 0$, as it is evident from Fig. 3. In addition, we have to include into consideration the phonon Hamiltonian H_{ph} [32–34],

$$H_{\text{ph}}(\mathbf{p}_{\mathbf{f}}, \mathbf{u}_{\mathbf{f}}) = \frac{1}{2M} \sum_{\mathbf{f}} \mathbf{p}_{\mathbf{f}}^2 + \frac{\kappa(b)}{2} \sum_{\mathbf{f}, \delta} [(\mathbf{u}_{\mathbf{f}, \delta} - \mathbf{u}_{\mathbf{f}}) \delta]^2 + \frac{\lambda(b)}{2} \sum_{\mathbf{f}, \delta} (\mathbf{u}_{\mathbf{f}, \delta} - \mathbf{u}_{\mathbf{f}})^2, \quad (33)$$

where $\kappa = U''(R_0)/2 - \lambda(R_0)$, $\lambda(R_0) = U'(R_0)/2R_0$, and $U(r)$ is the potential energy of interatomic interaction (Morse curve, see Fig. 2). As a result, the completed Hamiltonian of the monoatomic system at low temperature can be written as

$$\hat{H} = H_{\text{ph}} + \hat{H}_{\text{ss}} + \hat{H}_{\text{sph}}. \quad (34)$$

Thus, we can conclude that the dynamics of the spin subsystem is a principal factor in low-temperature properties of ${}^4\text{He}$. The term \hat{H}_{sph} describes spin-phonon coupling which has an effect on phonon spectrum of the condensed phase. The effect in some reasons is rather close to the mechanism of inelastic phonon scattering on the quadrupolar $o\text{-H}_2$ impurities in $p\text{-H}_2$ matrix [36,37].

6. Discussion

It is seen from Fig. 2 that the minimum of the ground-state potential curve is achieved at $R_{0\text{min}} = 0.875$, and this seems to be confusable in view of the fact that interatomic distance in liquid and solid helium is of order higher. However, we shall take into account that the potential well of Fig. 2 is essentially non-parabolic. The nuclear zero-point oscillations in this well have an equilibrium point $R_{\text{eq}} > R_0$, and the oscillations are essentially anharmonic, so that zero point energy can not be estimated directly through the curvature of potential energy curve at $R_0 = R_{0\text{min}}$. To comparison, we have shown on Fig. 2(a) the calculation from Ref. 21. To find the real internuclear distance in the ground state of He_2 dimer we have to solve the quantum mechanical problem which include nucleus degrees of freedom, and it will be a subject of further investigations.

The contact interaction term $\sim \hat{\sigma}_a \hat{\sigma}_b \delta(\mathbf{r}_a - \mathbf{r}_b)$ which is the main contribution to the spin-spin interaction in the ground state of an isolated two-electron helium atom [22,26–28], was used by Landau and Berestetskii [25] during studying the relativistic interaction between electron and positron (two one-half-spin elementary particles

with opposite charges). The delta-correlation of the particles is resulted by necessity of “cancellation of divergences” in formally divergent Coulomb integrals when calculating the matrix elements of interaction, it was clarified by authors of Ref. 25 in the conclusion of their paper. Note, that the cancellation of divergences is well-known problem of the quantum electrodynamics [35] which arises when calculating matrix elements for particles with Coulomb interactions. To include the operator $\hat{\sigma}_a \hat{\sigma}_b$ into the problem we have to be sure that the matrix element of $\delta(\mathbf{r}_a - \mathbf{r}_b)$ wave function of the ground state of helium atom [12] has non-zero value at arbitrary R_0 (see Fig. 3) which is quite evident in view of symmetry of the corresponding wave function describing the ground state of the helium atom, but the coefficient $8\pi/3$ is in reality only an estimation depending on the model of the δ -divergence cancellation. The spectrum of the single bilinear operator $\hat{\sigma}_a \hat{\sigma}_b$ consists of two states (singlet and triplet [18]) with eigenvalues -3 (singlet) and $+1$ (triplet), but only the parity of antisymmetric double-spin singlet state is compatible symmetric spatial ground level of an isolated helium atom. In addition, if the spin-spin correlation within the unitary shell of a stable helium atom makes its ground state lower, then the spin exchange in the pair of the electrons of the shell must be positive (antiferromagnetic), so that opposite to the negative exchange in electron-positron pair [25]. The presence of the spin-spin relativistic correction (of order $1/c^2$) for helium atom was discussed by different authors [22,26–28], but despite the evident difference in structure and properties between ${}^3\text{He}$ and ${}^4\text{He}$ this effect was not applied to discuss the spin contribution to interatomic interaction in condensed helium phases.

The situation is radically different for the pair exchange within four-spin cluster where antiferromagnetic nature of the exchange leads to the ground state as spin quintet with the parity complimentary to the complete ground-state wave function of the dimer. The exchange (of about 12 K) on the interatomic bond depends on the interatomic distance, so that there is a coupling between spin and phonon degrees of freedom which leads to renormalization of phonon spectrum in condensed phase as compared to the corresponding spinless medium. This effect can be interpreted as a direct analog of translation-rotation interaction in molecular cryocrystals [38–41].

7. Conclusions

It seems that spin-spin interaction as a part of the complete interatomic interaction (which is electromagnetic in its fundamental physical nature) in liquid and solid helium is the most essential to realize the observable physical properties of helium condensed phases at low temperatures. The spin-spin coupling appears as small $\sim 1/c^2$ relativistic correction to the main electrostatic

interaction, but at $T \rightarrow 0$ the corresponding effects play the principal role in the low-temperature phenomena. On the other hand, the matrix elements of the spin-spin exchange depend on charge distribution within the atomic system, so that there is a spin-phonon coupling as a factor of spin contribution in thermodynamics of the helium condensed matter. The spin-phonon interaction should be studied within a complex approach to description of the nuclear and electronic subsystems to obtain properly both the lattice dynamics corrected by relativistic contributions and matrix elements of the relativistic corrections complicated by Coulomb irregularities and contributions from nuclear degrees of freedom.

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1. J.O. Hirschfelder, Ch.F. Curtiss, and R.B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, NY (1954).
2. A.S. Rybalko, *Fiz. Nizk. Temp.* **30**, 1321 (2004) [*Low Temp. Phys.* **30**, 994 (2004)].
3. A.S. Rybalko and S.P. Rubets, *Fiz. Nizk. Temp.* **31**, 820 (2005) [*Low Temp. Phys.* **31**, 623 (2005)].
4. A. Rybalko, S. Rubets, E. Rudavskii, V. Tikhy, S. Tarapov, R. Golovashchenko, and V. Derkach, *Phys. Rev. B* **76**, 140503 (2007).
5. A. Rybalko, S. Rubets, E. Rudavskii, V. Tikhy, V. Derkach, and S. Tarapov, *J. Low Temp. Phys.* **148**, 527 (2007).
6. A.S. Rybalko, S.P. Rubets, E.Ya. 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)].
7. A.S. Rybalko, S.P. Rubets, E.Ya. 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)].
8. 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)].
9. 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).
10. N. Mott and I. Sneddon, *Wave Mechanics and its Applications*, Clarendon Press (1948).
11. P.M. Morse, *Phys. Rev.* **34**, 57 (1929).
12. T.N. Antsygina and K.A. Chishko, *Fiz. Nizk. Temp.* **40**, 1035 (2014) [*Low Temp. Phys.* **40**, 807 (2014)].
13. T.N. Antsygina and K.A. Chishko, *Fiz. Nizk. Temp.* **42**, 936 (2016) [*Low Temp. Phys.* **42**, 734 (2016)].
14. P.M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, NY (1953).
15. V.A. Fock, *Fundamentals of Quantum Mechanics*, MIR Publishers, Moscow (1979).
16. L.D. Landau, and E.M. Lifshitz, *Quantum Mechanics – Nonrelativistic Theory*, Pergamon Press (1965).
17. P. Gombás, *Theorie und Lösungsmethoden des Mehrteilchenproblems der Wellenmechanik*, Basel (1950).
18. S. Flügge, *Practical Quantum Mechanics II*, Springer (1971).
19. J. Frenkel, *Einführung in die Wellenmechanik*, Julius Springer, Berlin (1929).
20. D.A. Varshalovich, A.N. Moskalev, and V.K. Khersonski, *Quantum Theory of Angular Momentum*, World Scientific, Singapore (1988).
21. D. Sprecher, J. Liu, T. Krähenmann, M. Schäfer, and F. Merkt, *J. Chem. Phys.* **140**, 064304 (2014).
22. H.A. Bethe and E.E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Plenum, NY (1977).
23. V.B. Berestetskii, E.M. Lifshits, and L.P. Pitaevskii, *Relativistic Quantum Theory*, Vol. 1, Pergamon, NY (1971).
24. L.H. Thomas, *Nature* **117**, No. 2945, 514 (1926).
25. L.D. Landau and V.B. Berestetskii, *Sov. Phys.: ZhETP* **19**, 673 (1949).
26. W.A. Barker and F.N. Glover, *Phys. Rev.* **99**, 317 (1955).
27. J. Sucher and H.M. Foley, *Phys. Rev.* **95**, 966 (1954).
28. A.M. Sessler and H.M. Foley, *Phys. Rev.* **92**, 1321 (1953).
29. L.D. Landau, and E.M. Lifshitz, *Classical Field Theory*, Pergamon, NY (1971).
30. E.M. Lifshitz, and L.P. Pitaevsky, *Statistical Physics: Condensed State Theory*, Butterworth-Heinemann (1980).
31. T. Hill, *Statistical Mechanics*, McGraw-Hill, NY (1956).
32. T.N. Antsygina, M.I. Poltavskaya, and K.A. Chishko, *Fiz. Nizk. Temp.* **41**, 743 (2015) [*Low Temp. Phys.* **41**, 575 (2015)].
33. K.A. Chishko, T.N. Antsygina, and M.I. Poltavskaya, *J. Low Temp. Phys.* **187**, 468 (2017).
34. K.A. Chishko, *Fiz. Nizk. Temp.* **44**, 154 (2018) [*Low Temp. Phys.* **44**, 114 (2018)].
35. A.I. Akhiezer and V.B. Berestetskii, *Quantum Electrodynamics*, John Wiley & Sons, NY (1965).
36. T.N. Antsygina, V.A. Slusarev, and K.A. Chishko, *J. Exp. Theor. Phys.* **87**, 303 (1998).
37. T.N. Antsygina, K.A. Chishko, and V.A. Slusarev, *J. Low Temp. Phys.* **111**, 503 (1998).
38. T.N. Antsygina and V.A. Slyusarev, *Teor. Math. Fiz.* **77**, 234 (1988).
39. T.N. Antsygina, M.I. Poltavskaya, and K.A. Chishko, *Fiz. Tverd. Tela* **44**, 1215 (2002).
40. T.N. Antsygina, M.I. Poltavskaya, and K.A. Chishko, *Fiz. Nizk. Temp.* **29**, 961 (2003) [*Low Temp. Phys.* **29**, 720 (2003)].
41. T.N. Antsygina, M.I. Poltavskaya, K.A. Chishko, T.A. Wilson, and O.E. Vilches, *Fiz. Nizk. Temp.* **35**, 1323 (2004) [*Low Temp. Phys.* **35**, 1081 (2004)].
42. It should be noted that Eq. (9) gives correct expression of $\mathcal{R}_{nl}(r)$ through Laguerre polynomials L_{n-l-1}^{2l+1} in determination given by V.A. Fock [15]. In a number literature sources [17,22] we can see unsatisfactory representation as L_{n+l}^{2l+1} . The correct polynomial representation for hydrogen-like radial wave function was derived by V.A. Fock [15].

Низькоенергетичні збудження у гелієподібному димері в рамках методу точної діагоналізації

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Методом точної діагоналізації (розкладанням за усеченим ортонормованим базисом) строго вирішено нерелятивістську квантовомеханічну задачу про зв'язані стани чотирьох взаємодіючих безспінових електронів, що рухаються в кулонівському полі двох точкових центрів тяжіння з $Z_0 = 2$, розташованих на фіксованій відстані R_0 (димер ${}^4\text{He}_2$ в наближенні Борна–Оппенгеймера–Гейтлера–Лондона). Розраховано чотириспінові релятивістські поправки (порядку $\sim 1/c^2$) до рівня основного стану димера з точною діагоналізацією спінового кластера, спектром та власними векторами спінової задачі. Показано, що парний спіновий зв'язок є антиферромагнітним з обмінною константою в 12 К (вона забезпечує антисиметрію спінової синглетної хвильової функції основного стану для ізольованого атома ${}^4\text{He}$ з двома ферміонами, пов'язаними всередині унітарної просторово-симетричної оболонки). Однак в чотириелектронній оболонці димера ${}^4\text{He}_2$ цей факт призводить до квінтетного основного стану чотириспінового кластера, який повністю антисиметричний щодо парних перестановок. Обмінна взаємодія всередині міжатомного зв'язку залежить від міжатомної відстані, так що існує зв'язок між спіновими та фононними рівнями свободи, що призводить до перенормування фононного спектра в конденсованій фазі в порівнянні з відповідним безспіновим середовищем. Цей ефект можна інтерпретувати як прямий аналог трансляційно-обертової взаємодії в молекулярних крио кристалах.

Ключові слова: міжатомна взаємодія He–He, релятивістські поправки, спин–спінова взаємодія.

Низкоенергетические возбуждения в гелиеподобном димере в рамках метода точной диагонализации

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Методом точной диагонализации (разложения по усеченному ортонормированному базису) строго решена нерелятивистская квантовомеханическая задача о связанных состояниях четырех взаимодействующих бесспиновых электронов, движущихся в кулоновском поле двух точечных центров притяжения с $Z_0 = 2$, расположенных на фиксированном расстоянии R_0 (димер ${}^4\text{He}_2$ в приближении Борна–Оппенгеймера–Гейтлера–Лондона). Рассчитаны четырехспиновые релятивистские поправки (порядка $\sim 1/c^2$) к уровню основного состояния димера с точной диагонализацией спинового кластера, спектром и собственными векторами спиновой задачи. Показано, что парная спиновая связь является антиферромагнитной с обменной константой в 12 К (она обеспечивает антисимметрию спиновой синглетной волновой функции основного состояния для изолированного атома ${}^4\text{He}$ с двумя фермионами, связанными внутри унитарной пространственно-симметричной оболочки). Однако в четырехэлектронной оболочке димера ${}^4\text{He}_2$ этот факт приводит к квинтетному основному состоянию четырехспинового кластера, которое полностью антисимметрично относительно парных перестановок. Обменное взаимодействие внутри межатомной связи зависит от межатомного расстояния, так что существует связь между спиновыми и фононными уровнями свободы, что приводит к перенормировке фононного спектра в конденсированной фазе по сравнению с соответствующей безспиновой средой. Этот эффект можно интерпретировать как прямой аналог трансляционно-вращательного взаимодействия в молекулярных крио кристаллах.

Ключевые слова: межатомное взаимодействие He–He, релятивистские поправки, спин–спиновое взаимодействие.