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ESTIMATES FOR THE INTERACTION POTENTIAL BETWEEN TWO ATOMS

V. A. Malyshev* **and R. A. Minlos†**

We consider a quantum system consisting of two electrons in the Coulomb field of two immovable nuclei spaced at a fixed distance, which is considered the problem parameter. We use spectral theory methods to obtain estimates of the system ground-state energy as a function of the internuclear distance. We obtain part of the results under the assumption that the Coulomb interaction constant between different atoms is small. We discuss the importance of the presented investigation for quantum chemistry.

Keywords: spectrum of the Schrödinger operator, quantum chemistry, hydrogen molecule

1. Introduction

This paper is devoted to a single mathematical problem: obtaining detailed information about the structure of solutions in the restricted quantum four-body problem. This is the first problem in a circle of problems connected with the fundamental question in quantum chemistry: What is the interaction between atoms? Such problems have always been outside the mainstream of the development of the theory and have not received sufficient attention from mathematicians although these problems are closely related to the two thoroughly investigated divisions of spectral analysis for Schrödinger operators, scattering theory and bound state theory.

It is commonly accepted that atoms should be treated exclusively at the quantum level. The bound states are found for one-electron atoms and ions explicitly, and there are many approximate methods for estimating them for many-electron atoms. It would seem also natural to treat molecules as purely quantum systems consisting of several nuclei and electrons. One obstacle to this is the calculation complexity, and there are no explicit calculations of eigenfunctions or eigenvalues even for a hydrogen molecule or ion. In other words, the situation for molecules differs essentially; it resembles the situation in celestial mechanics, where the three-body problem also admits no explicit solution. These conditions have led to a strange mixture of approximate quantum and classical approaches in molecular physics. Moreover, in parallel with the long existing, entirely computational quantum chemistry, there have appeared new developing computational sciences such as molecular dynamics or molecular mechanics, which simulate a large molecule as a system of classical particles with some artificially introduced two-particle potentials. The question of where these potentials should be taken and also the more general question of where the various potentials used at the microlevel in statistical physics should be taken (e.g., the Lennard-Jones potential and the quadratic potential of harmonic oscillators) to investigate the microscopic properties of a substance remains open at the mathematical level. At the same time, the only fundamental "legitimate" potential is the Coulomb potential (if the magnetic properties and the spin are neglected). It is natural to ask whether this multitude of potentials can be derived from the Coulomb potential. Although this

*Lomonosov Moscow State University, Moscow, Russia, e-mail: malyshev2@yahoo.com.

†Kharkevich Institute for Information Transmission Problems, RAS, Moscow, Russia, e-mail: minl@iitp.ru.

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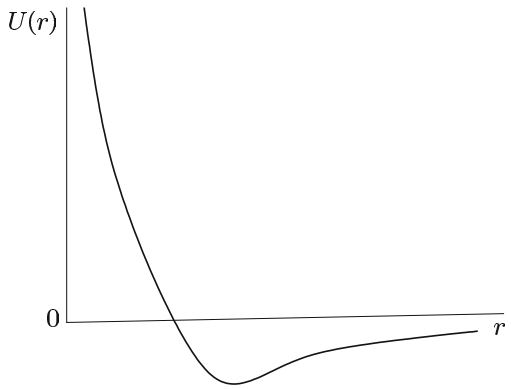

Fig. 1. Typical form of interaction.

question has undoubtedly been widely discussed in physics, we are unfamiliar with any rigorous results of this kind.

There are also other similar questions without answers. For example, chemists and also physicists (see, e.g., [1]) treat atoms as molecular components that nevertheless do not lose their individuality. A natural question arises: What does it mean that "atoms" are identified in a system of nuclei and electrons? Another question is whether we can give exact definitions for various kinds of chemical bonds, such as covalent, ion, and hydrogen bonds.

The approach usually used in physics and quantum chemistry (see, e.g., [2]–[4]) is as follows. For two neutral atoms with Z_1 and Z_2 electrons, we consider a restricted problem in which the corresponding nuclei are fixed at a distance x from each other, and we calculate the least eigenvalue $E(x)$ of the system of Z_1+Z_2 electrons in the field of the two immovable nuclei. The interaction energy of the two atoms separated by a distance x is then understood to be

$$U(x) = E(x) - E_{0,1} - E_{0,2} + \frac{Z_1 Z_2 e^2}{|x|}, \tag{1}$$

where $E_{0,i}$ is the ground state energy of the ith atom, $Z_i e$ is the charge of the ith nucleus, and the third term in the right-hand side corresponds to the Coulomb internuclear interaction. Part of our results relate to the case $Z_1 = Z_2 = 1$, and a small constant α is introduced before the Coulomb interaction between different atoms for the rest.

The primary question is about the reasonability of the definition itself. If this definition (somehow averaged over x) seems natural for bound states, i.e., for two-atom molecules, then it is a priori totally unclear how it relates to scattering or, generally, to the relative dynamics of two atoms. The justification of the latter relation is usually connected with the Born–Oppenheimer adiabatic approximation. There is an extensive physical literature on this subject (see, e.g., [5]), but the mathematical justification has been obtain only in the framework of the semiclassical approximation (see, e.g., [6]–[9]).

The next question, about the qualitative behavior of the function $U(x)$, was resolved in the framework of computer calculations because there are unsolved problems even in the case of immovable nuclei: while the restricted three-body problem has explicit solutions in celestial mechanics, this is not so in the quantum case (but see [10] for the case of two electrons in the field of two nuclei).

Here, we consider a system of two hydrogen atoms, i.e., $Z_1 = Z_2 = 1$. We prove several results confirming the typical form of interaction presented in many monographs on quantum chemistry (see, e.g., [2]) and shown in Fig. 1. We note that the Lennard-Jones potential

$$U_{\mathrm{LJ}} = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right),$$

where $\epsilon, \sigma > 0$ are parameters, has the same qualitative behavior. Of course, the above formula cannot be derived accurately; in particular, such a rapid increase at zero cannot be obtained. Therefore, we can only speak about the qualitative behavior. Three features are fundamental: the rate of increase at zero, the rate of decrease at infinity, and the existence of a single minimum.

2. Results

We consider a quantum system consisting of two nuclei (protons) fixed at the points 0 and x in the space $\mathbb{R}^3$ and two electrons in the field of these nuclei. Let y be the position of the first electron and $x+z$ be that of the second. The Hamiltonian of the system in the space $\mathbf{H} = L_2(\mathbb{R}^6) = L_2(\mathbb{R}^3) \otimes L_2(\mathbb{R}^3)$ is

$$H = H(\alpha, x) = H_{0,y} \otimes 1 + 1 \otimes H_{0,z} + \alpha V(y, z),$$

where

$$H_{0,y} = -\Delta_y - \frac{1}{|y|}, \qquad H_{0,z} = -\Delta_z - \frac{1}{|z|}$$

are the Hamiltonians of the hydrogen atoms with nuclei fixed at the respective points 0 and x. The interaction between the particles of different atoms is given by the operator of multiplication by the function

$$V(y, z) = V_x(y, z) = \frac{1}{|x|} - \frac{1}{|x-y|} - \frac{1}{|x+z|} + \frac{1}{|x-y+z|},$$

where the proton and electron charges are assumed to be $+1$ and -1. The parameter $\alpha \geq 0$ is equal to unity in the physical case.

If we let $E_0/2$ denote the ground-state energy of the hydrogen atom, then $H(0, x)$ also has a single nondegenerate bound state Ψ_0 with the energy $E_0 = E_0(x)$, which is, of course, independent of x. As is well known [11], the ground state of the hydrogen atom is determined by the wave function (we assume that the nucleus is located at the point 0)

$$\varphi(y) = \frac{1}{\sqrt{\pi}} e^{-|y|} \in L^2(\mathbb{R}^3), \tag{2}$$

and consequently

$$\Psi_0 = \varphi(y)\varphi(z) = \frac{1}{\pi} e^{-|y|-|z|}. \tag{3}$$

We note that the term $\alpha/|x|$ in the Hamiltonian is a constant number, and it is convenient to state some properties in terms of the Hamiltonian with the internuclear interaction excluded,

$$H_{\text{electron}} = H_{\text{electron}}(\alpha, x) = H - \alpha \frac{1}{|x|},$$

i.e., the Hamiltonian of a system of two electrons in the field of two nuclei.

We first present some known facts about the Hamiltonian H_{electron}.

1. The Hamiltonian H_{electron} is essentially self-adjoint on C_0^∞ for all x and all α and is bounded below and moreover uniformly bounded with respect to x for a given α (see Theorems X.12, X.15, and X.16 in [12] and also [6]).

2. For $\alpha > 0$, the essential spectrum of H_{electron} fills the half-axis $[\mu, \infty)$, where $\mu = \mu(\alpha, x) < 0$, and the discrete spectrum consists of infinitely many eigenvalues on the half-interval $[E_\alpha^{\text{electron}}(x), \mu)$ that converge to μ (see [13]), where $E_\alpha^{\text{electron}}(x)$, the infimum of the spectrum of the Hamiltonian $H_{\text{electron}}(\alpha, x)$, is the least eigenvalue of H_{electron} and moreover nondegenerate (see [12], [14], [15]).

We let

$$E_\alpha(x) = E_\alpha^{\text{electron}} + \alpha\frac{1}{|x|}$$

denote the least eigenvalue of H. It is important for determining the interatomic interaction, which is defined in accordance with (1) as

$$U(x) = U^{(\alpha)}(x) = E_\alpha(x) - E_0(x) = E_\alpha(x) - E_0.$$

Because of the spherical symmetry, we have $E_\alpha(x) = E_\alpha(r)$, i.e., $E_\alpha(x)$ depends only on $r = |x|$, and we use both notations where it does not lead to misunderstanding.

It can be easily verified that the set of the operators $H(\alpha, x)$ for a fixed x is an entire analytic family (in the sense of Kato) in the neighborhood of the point $\alpha = 0$ (see Theorems X.12, X.15, and X.16 in [12]). By the Kato–Rellich theorem, for small values of α, there exists a unique nondegenerate eigenvalue $E_\alpha(x)$ in some neighborhood of the point $E_0(x)$ (see Vol. 4 of [12]). And it can be expanded in the Rayleigh–Schrödinger series

$$E_\alpha(r) = E_0 + \sum_{n=1}^{\infty} \alpha^n c_n(r), \tag{4}$$

which converges for small α.

Lemma 1. *There is an $\alpha_0 > 0$ such that series (4) converges uniformly in x for $|\alpha| \le \alpha_0$.*

Theorem. 1. *The relation*

$$U(r) = \frac{\alpha}{r} + O(1), \quad r \to 0,$$

holds for all $\alpha > 0$.

2. *For an arbitrary r, the first coefficient in series (4) has the form*

$$c_1(r) \doteq \lim_{\alpha\to 0} \frac{E_\alpha(r) - E_0}{\alpha} = \frac{1}{r} - \frac{1 - e^{-2r}}{r} - \frac{e^{-2r}}{6}\left(r^2 + \frac{9}{2}r + \frac{81}{4}\right) =$$

$$= e^{-2r}\left(\frac{1}{r} - \frac{1}{6}\left(r^2 + \frac{9}{2}r + \frac{81}{4}\right)\right). \tag{5}$$

The function $c_1(r)$ has a single (nondegenerate) minimum on the interval $(0, \infty)$, decreases exponentially as $r \to \infty$, and increases as $1/r$ as $r \to 0$. Moreover, the full interaction $U(r)$ also has a single minimum for small α.

3. *The second coefficient in the perturbation theory satisfies the inequalities*

$$\frac{D_1}{r^6} < -c_2(r) < \frac{D_2}{r^6}, \tag{6}$$

where $0 < D_1 < D_2 < \infty$ are some constants.

4. *For all $\alpha > 0$ and sufficiently large r, we have*

$$-U(r) < \frac{C}{r^6}$$

for some constant $C = C(\alpha) > 0$.

The electron spin is not taken into account in the model we consider here, but similar calculations can also be performed with the spin included.

3. Proof of the theorem

3.1. The first statement in the theorem: Small values of $|x|$. We consider the function H_{electron}, i.e., the Hamiltonian of two electrons in the field of two nuclei fixed at the origin and at the point x. If these nuclei are at the same point, i.e., $x = 0$ and $\alpha = 1$, then this is a helium atom. For small α, it is natural to take the internuclear distance r as a perturbation parameter. In this case, it is known that for this problem with two electrons in the field of two centers, the Hamiltonian $H_{\text{electron}}(x)$ is bounded below uniformly in x, and the least eigenvalue exists [13], is nondegenerate [14], [15], and depends smoothly on x [6]. Hence, the only increasing contribution to $U(x)$ at zero is given by the internuclear interaction, i.e., by α/r.

3.2. The second statement in the theorem.

3.2.1. Electrostatic interaction. We let $\rho(y) = |\varphi(y)|^2$ denote the probability density for the ground state to have an electron at the point $y \in \mathbb{R}^3$. In the corresponding system of units, $\rho(y)$ is then the charge density of the "electron cloud," and by (2), we have

$$\rho(y) = \frac{1}{\pi}\, e^{-2|y|}. \tag{7}$$

Therefore, the hydrogen atom can be regarded as a charge system, and the interaction between the two atoms can be treated as the Coulomb interaction between two such charge systems. Namely, let μ_1 and μ_2 be two finite measures in the space $\mathbb{R}^3$ with a zero total charge, i.e.,

$$\int |d\mu_i| < \infty, \qquad \int d\mu_i = 0, \quad i = 1, 2.$$

By the electrostatic interaction (or two-potential) between these measures, we mean the function

$$U_{\text{es}}(x) = \alpha \int \frac{1}{|x + z - y|}\, d\mu_1(y)\, d\mu_2(z), \quad x \in \mathbb{R}^3. \tag{8}$$

In our case, we have

$$d\mu_1(y) = d\mu_2(y) = \delta(y) + \rho\, dy,$$
$$U_{\text{es}}(x) = \alpha(U_{00}(x) + U_{01}(x) + U_{10}(x) + U_{11}(x)),$$

where the four terms in the above formula are defined as follows: the interaction between the two nuclei located at the points 0 and x is

$$U_{00}(x) = \frac{1}{|x|},$$

the interaction between the nucleus of the first atom and the electrons of the second atom is

$$U_{01} = -\int \frac{1}{|x - y|}\rho(y)\, dy,$$

the interaction between the nucleus of the second atom and the electrons of the first atom is

$$U_{10} = -\int \frac{1}{|x + z|}\rho(z)\, dz,$$

and, finally, the interaction between the electrons of different atoms is

$$U_{11} = \int \frac{1}{|x-y+z|}\rho(y)\rho(z)\,dy\,dz.$$

A special case of the two-potential is the main definition in potential theory (see [16]): the function

$$U_{\text{potential}}(x) = \int \frac{1}{|x-y|}\,d\mu_1(y), \quad x \in \mathbb{R}^3,$$

is called the potential (or one-potential) of the measure μ_1. It is obtained from expression (8) if the function $\mu_2(z)$ is taken equal to $\delta(z)$, i.e., to the unit measure at the point 0. This coincides with the electric potential created by the measure μ_1,

$$U_{\text{potential}}(x) = U_{00} + U_{01} = \frac{1}{|x|} - \int \frac{1}{|x-y|}\rho(y)\,dy.$$

In this case, we have

$$U_{\text{es}}(x) = \alpha \int U_{\text{potential}}(x)\,d\mu_1(x) = \alpha U_{\text{potential}}(x) - \alpha \int U_{\text{potential}}(x-z)\,d\rho(z).$$

We also note that as follows from formula (3) and the results in [12], $U_{\text{es}}(r)$ coincides with the first term of series (4),

$$U_{\text{es}}(r) = \alpha c_1(r) = (\Psi_0, \alpha V(r)\Psi_0).$$

3.2.2. A crude estimate for the rate of decrease. We first show that $U_{\text{es}}(x)$ decreases faster than any power of r^{-1} using a simple and visual method, and we then present a less intuitive derivation of the expression for $c_1(r)$. We prove the following lemma.

Lemma 2. *If both the hydrogen atoms are in the ground state, then $U_{\text{es}}(x)$ decreases faster than any power r^{-N} as $x \to \infty$.*

Proof. It suffices to prove that for an arbitrary positive integer $N > 0$, the function $U_{\text{potential}}(x)$ decreases faster than r^{-N}. For this, we use the asymptotic (multipole) expansion for large r (see, e.g., [17])

$$\int \frac{\rho(z)}{|x-z|}\,dz = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{4\pi}{2l+1}\frac{1}{r^{l+1}}Y_{lm}(\vartheta,\varphi)Q_{lm},$$

where $Y_{lm}(\vartheta,\varphi)$ are spherical functions and

$$Q_{lm} = \int Y^*_{lm}(\vartheta,\varphi)r^l\rho(r)\,dz, \qquad dz = \sin\vartheta\,d\varphi\,d\vartheta\,r^2\,dr.$$

As usual, this expansion means that the finite sum $\sum_{i=0}^{N}$ differs from the left-hand side by $O(r^{-N-1})$. On the other hand, by the spherical symmetry of $\rho(r)$, all coefficients Q_{lm} are zero except the coefficient Q_{00}, which is equal to $1/\sqrt{2\pi}$. Because we also have $Y_{00} = 1/\sqrt{2\pi}$, we see that the asymptotic series consists of a single term $1/r$, which proves our assertion about the rate of decrease of $U_{\text{potential}}(r)$.

3.2.3. Derivation of formula (5). In what follows, we assume that the point x lies on the positive part of the first of the axes 1, 2, and 3 in the space $\mathbb{R}^3$. The derivation reduces to direct calculations. In our case, we have

$$U_{11}(x) = \frac{1}{\pi^2}\int_{y+u+v=x} \frac{e^{-2|y|-2|v|}}{|u|}\,dy\,du\,dv,$$

$$U_{01}+U_{10} = -\frac{2}{\pi}\int \frac{e^{-2|y|}}{|x-y|}\,dy.$$

We consider the Fourier transforms of these two integrals,

$$I_1(p) = \widetilde{U}_{11}(p) = \int e^{i(p,x)}U_{11}(x)\,dx = \frac{1}{\pi^2}\varphi_1^2(p)\psi(p),$$

$$I_2(p) = -\frac{2}{\pi}\int e^{i(p,x)}\int \frac{e^{-2|y|}}{|x-y|}\,dy\,dx,$$

where

$$\varphi_1(p) = 2\pi\int_{\mathbb{R}^3} e^{i(p,x)}e^{-2|y|}\,dy, \qquad \psi(p) = \int \frac{e^{i(p,x)}}{|y|}\,dy.$$

We introduce the spherical coordinates in which $-\pi/2 \le \phi \le \pi/2$ is the angle between the vector x and the x_1 axis, and $-\pi \le \vartheta \le \pi$ is the angle between the vector z and the Ox_2x_3 plane. We then have

$$\varphi(p) = 2\pi\int_0^\infty r^2\int_0^\pi d\vartheta\,\sin\vartheta\,e^{ir|p|\cos\vartheta-2r}\,dr = \frac{16\pi}{(p^2+4)^2},$$

$$\psi(p) = \int \frac{e^{i(p,x)}}{|y|}\,dy = \frac{4\pi}{|p|^2}.$$

Hence,

$$-I_1(p) = \frac{2^{10}\pi}{p^2(p^2+4)^4}, \qquad I_2(p) = \frac{2^7\pi}{p^2(p^2+4)^2}.$$

We now calculate the inverse Fourier transforms. Writing $s = |p|$ and, as usual, $r = |x|$ and also introducing the spherical coordinates, we obtain

$$\begin{aligned}
-(U_{01}(x)+U_{10}(x)) &= \frac{1}{8\pi^3}\int e^{-i(x,p)}I_2(p)\,dp = \\
&= \frac{16}{\pi}2\int_0^\infty s^2\,ds\int_0^\pi d\vartheta\,\sin\vartheta\frac{e^{irs\cos\vartheta}}{s^2(s^2+4)^2} = \\
&= \frac{16}{\pi r}2\int_0^\infty ds\,\frac{e^{irs}-e^{-irs}}{is(s^2+4)^2} = \frac{16}{\pi r}2\int_{-\infty}^\infty ds\,\frac{e^{irs}-e^{-irs}}{3is(s^2+4)^2} = \\
&= \frac{2^5}{\pi r 2i}2\pi i\left(\frac{1}{2^4}+\operatorname{Res}\left(\frac{e^{irs}}{s(s^2+4)^2}\right)\Big|_{s=2i}+\operatorname{Res}\left(\frac{e^{-irs}}{s(s^2+4)^2}\right)\Big|_{s=-2i}\right) = \\
&= \frac{2^5}{r}\left(\frac{1}{2^4}+\left(\frac{e^{irs}}{s(s+2i)^2}\right)'\Big|_{s=2i}+\left(\frac{e^{-irs}}{s(s-2i)^2}\right)'\Big|_{s=-2i}\right) = \\
&= \frac{2^5}{r}\left(\frac{1}{2^4}+\frac{r}{2^4}e^{-2r}-\frac{e^{-2r}}{2^4}\right) = -2\left(e^{-2r}+\frac{1-e^{-2r}}{r}\right).
\end{aligned}$$

Similarly calculating the other integral, we obtain

$$U_{11}(x) = \frac{1}{8\pi^3}\int e^{-i(x,p)} I_1(p)\,dp = \frac{1-e^{-2r}}{r} - \frac{e^{-2r}}{6}\left(r^2 + \frac{9}{2}r + \frac{33}{4}\right),$$

whence (5) follows.

In particular, the resulting explicit expression implies that $U_{\rm es}(r)$ decreases exponentially at infinity.

3.2.4. The proof of Lemma 1. We essentially use the technique related to the famous Kato inequality here (see [18], [12]). For the proof, we note that the function $1/|\xi|$ can be represented as a sum of two functions,

$$\frac{1}{|\xi|} = \phi_1(\xi) + \phi_2(\xi),$$

where $\phi_1(\xi) \in L_2(\mathbb{R}^3)$ and $\phi_2(\xi) \in L_\infty(\mathbb{R}^3)$. Using the method in the proof of Theorem X.16 in [12] (also see Example 2 in Vol. 2 of [12]), we then obtain

$$\left\|\left(\frac{1}{|y|} + \frac{1}{|z|}\right) f\right\|_{L_2(\mathbb{R}^6)} < a\|(\Delta_y + \Delta_z) f\|_{L_2(\mathbb{R}^6)} + b\|f\|_{L_2(\mathbb{R}^6)} \tag{9}$$

for $f \in C_\infty(\mathbb{R}^6)$, where $a, b > 0$ are some constants and the constant a can be chosen arbitrarily small. Similarly,

$$\left\|\alpha\left(-\frac{1}{|x-y|} - \frac{1}{|x+z|} + \frac{1}{|x-y+z|}\right) f\right\|_{L_2(\mathbb{R}^6)} < \alpha a\|(\Delta_y + \Delta_z) f\|_{L_2(\mathbb{R}^6)} + \alpha b_1\|f\|_{L_2(\mathbb{R}^6)}. \tag{10}$$

It follows from (9) that the operator

$$H_0 = -\Delta_y - \Delta_z - \frac{1}{|y|} - \frac{1}{|z|}$$

satisfies the estimate

$$\|H_0 f\|_{L_2(\mathbb{R}^6)} + a\|(\Delta_y + \Delta_z) f\|_{L_2(\mathbb{R}^6)} + b\|f\|_{L_2(\mathbb{R}^6)} > \|(\Delta_y + \Delta_z) f\|_{L_2(\mathbb{R}^6)},$$

i.e., the inequality

$$\|(\Delta_y + \Delta_z) f\|_{L_2(\mathbb{R}^6)} < \frac{1}{1-a}(\|H_0 f\|_{L_2(\mathbb{R}^6)} + b\|f\|_{L_2(\mathbb{R}^6)})$$

holds. Substituting this inequality in (10), we obtain

$$\left\|\alpha\left(-\frac{1}{|x-y|} - \frac{1}{|x+z|} + \frac{1}{|x-y+z|}\right) f\right\|_{L_2(\mathbb{R}^6)} < a_2\|H_0 f\|_{L_2(\mathbb{R}^6)} + b_2\|f\|_{L_2(\mathbb{R}^6)}, \tag{11}$$

where

$$b_2 = \frac{\alpha a}{1-a} b + \alpha b_1, \qquad a_2 = \frac{\alpha a}{1-a}.$$

For small a, we have $\alpha a/(1-a) < 1$, and the two constants a_2 and b_2 are independent of x. It follows from inequality (11) that the operator $H_{\rm electron}$ is self-adjoint and is bounded below. In this case, the Rayleigh–Schrödinger series for the lower eigenvalue of this operator differs from the corresponding series for the eigenvalue of the operator $H(\alpha, x)$ only in the constant $\alpha/|x|$, and these series consequently have the same convergence radius R_0. Using Theorem XII.11 in [12], we obtain the estimate

$$R_0 \geq \left[a_2 + \epsilon_0^{-1}[b_2 + a_2(|E_0| + \epsilon_0)]\right]^{-1} = R_{\rm lower},$$

where ϵ_0 is the half-distance from the minimal eigenvalue to the remaining spectrum. The right-hand side of this inequality is independent of x. Because the convergence rate of a power series converging inside some circle is determined by the radius of the circle, we conclude that the series in question converges uniformly in x. The lemma is proved.

3.2.5. The end of the proof of the second statement in the theorem. As previously noted, the first term in expansion (4) has the form

$$\alpha c_1(r) = U_{\text{es}} = \alpha(\Psi_0, V\Psi_0) \tag{12}$$

and coincides with the electrostatic (classical) interatomic interaction $U_{\text{es}}(r)$ introduced above. We see that the function $U_{\text{es}}(r)$ is of the order of α/r as $r \to 0$ and that the absolute value of $U_1(r)$ decreases exponentially as $r \to \infty$. Because the expression in the parentheses in the right-hand side of the formula

$$U_{\text{es}}(x) = \alpha e^{-2r}\left(\frac{1}{r} - \frac{1}{6}\left(r^2 + \frac{9}{2}r + \frac{81}{4}\right)\right)$$

is the difference between a decreasing function and an increasing function and U_{es} has different signs in the neighborhood of zero and at infinity, the function $U_{\text{es}}(x)$ has a single zero for $x > 0$. As can be shown by a simple calculation, the derivative $U'_{\text{es}}(x)$ can also be represented similarly and hence also has a single zero at some point $x_{\min} > 0$. Therefore $U_{\text{es}}(x)$ has a single minimum $U_{\text{es}}(x_{\min)}) < 0$. It can be shown that this minimum is nondegenerate.

It was proved in [6] that the least eigenvalue $E_\alpha(x)$ of the operator H is twice differentiable with respect to r and the first and second derivatives $E'_\alpha(x)$ and $E''_\alpha(x)$ can be expanded in power series in α that are obtained by differentiating series (4) with respect to r. This and the uniform convergence of series (4) imply that the full interaction has a single minimum for sufficiently small α.

3.3. The third statement in the theorem.

3.3.1. The lower estimate for the second coefficient in the perturbation theory. For large r, the "small parameter" is $\beta = r^{-1}$. Although the operator V formally disappears at $\beta = 0$, the parameter β is involved in the perturbation nonlinearly, which leads to some difficulties.

For small α, the second coefficient in the perturbation theory has the form (see Sec. XII.2 in [12])

$$\begin{aligned} c_2 &= -\int_{|\lambda - E_0| > \epsilon_0} (\lambda - E_0)^{-1}\, d(VX_0, P_\lambda VX_0) = \\ &= -\left(VX_0, \int_{|\lambda - E_0| > \epsilon_0} (\lambda - E_0)^{-1}\, dP_\lambda VX_0\right) = \\ &= -(VX_0, (\lambda - H_0)^{-1}(1 - P_0)VX_0), \end{aligned} \tag{13}$$

where we set $X_0 = \Psi_0$. This implies

$$|c_2| \le \|(H_0 - E_0)^{-1}(1 - P_0)\|\, \|VX_0\|^2 \le C_0 \|VX_0\|^2,$$

where C_0 is the norm of the operator $(H_0 - E_0)^{-1}$ on the subspace orthogonal to X_0.

We estimate the asymptotic expression for the norm of VX_0 at small β, for which we split the range of each variable y and z into two regions. For example, in the case of y, we split the range as

$$|y| \le |x|^\delta, \qquad |y| > |x|^\delta,$$

where $\delta > 0$ is sufficiently small, and we then write

$$A_{11} = \{(y, z)\colon |y| \le |x|^\delta, |z| \le |x|^\delta\}, \qquad A_{12} = \{(y, z)\colon |y| \le |x|^\delta, |z| > |x|^\delta\},$$

and so on. In this case, the function $\varphi(y)$ is represented in the form

$$\varphi(y) = \varphi_1(y) + \varphi_2(y), \qquad \varphi_1(y) = \varphi(y)\mathbf{1}_{|y|\le|x|^\delta}, \qquad \varphi_2(y) = \varphi(y)\mathbf{1}_{|y|>|x|^\delta},$$

and a similar representation is obtained for $\varphi(z)$. In this case, $\|VX_0\|^2$ splits into 16 summands,

$$\|VX_0\|^2 = (VX_0, VX_0) = \sum_{i,j,k,l} a_{ij,kl}, \qquad a_{ij,kl} = (VX_{ij}, VX_{kl}), \quad i,j,k,l = 1,2,$$

where $X_{ij} = \varphi_i(y)\varphi_j(z)$. Here, only the terms $a_{ij,kl}$ with $(i,j) = (k,l)$ turn out to be nonzero. We first consider the term $a_{11,11}$ corresponding to the region A_{11}. If the coordinates x_1, x_2, x_3 are chosen such that the vector x lies on the x_1 axis, then it is convenient to represent V in the form

$$V = V(\beta) = \beta\biggl(1 - \frac{1}{\sqrt{1 - 2y_1\beta + \beta^2|y|^2}} - \frac{1}{\sqrt{1 + 2z_1\beta + \beta^2|z|^2}} + \\ + \frac{1}{\sqrt{1 + 2(z_1 - y_1)\beta + \beta^2|z-y|^2}}\biggr) = B_1\beta + B_2\beta^2 + B_3\beta^3 + R_3(\beta)$$

with the integral expression

$$R_3(\beta) = \frac{1}{6}\int_0^\beta (\beta - t)^3 V^{(4)}(t)\,dt$$

for the remaining terms. It is easy to show that

$$B_1 = B_2 = 0, \qquad B_3 = B_3(y,z) = -\frac{1}{2}(y,z) - 6y_1z_1.$$

Therefore, we can write the interaction as

$$V = \beta^3 B_3 + R_3(\beta). \tag{14}$$

Some simple calculations show that for $0 < t < \beta$ and $(y,z) \in A_{11}$, the expression $V^{(4)}(t;y,z)$ admits the estimate

$$|V^{(4)}(t;y,z)| < \text{const} \cdot (|y|^3 + |z|^3).$$

It follows that

$$|R_3(\beta;y,z)| < \text{const} \cdot \beta^4(|y|^3 + |z|^3).$$

Because we have the estimates

$$0 < \int_{A_{11}} [\beta^3 B_3(y,z)\varphi_1(y)\varphi_1(z)]^2\,dy\,dz < \\ < \beta^6 \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} B_3^2(y,z)\varphi^2(y)\varphi^2(z)\,dy\,dz = \frac{C_{11}}{r^6},$$

where $C_{11} > 0$ is a constant, and

$$\int_{A_{11}} |\beta^3 B_3(y,z)R_3(y,z)|[\varphi_1(y)\varphi_1(z)]^2\,dy\,dz = O(r^{-7}),$$

$$\int_{A_{11}} |R_3(y,z)|^2[\varphi_1(y)\varphi_1(z)]^2\,dy\,dz = O(r^{-8}),$$

we obtain

$$(VX_{11}, VX_{11}) < \frac{C_{11}}{r^6}.$$

The other terms $a_{ij,kl}$ contain at least one function φ_2 with an estimate $e^{-|x|^\delta}$ in the integrand. For example, we consider the term

$$a_{12,12} = \int_{A_{12,12}} V^2(y,z)\varphi_1^2(y)\varphi_2^2(z)\,dy\,dz,$$

which in turn consists of nine integrals appearing as V is squared. Three of them, for example, the term

$$J_1 = \iint \frac{1}{|x-y|^2}\varphi_1^2(y)\varphi_2^2(z)\,dy\,dz,$$

involve the square of the interaction. This term is estimated as

$$|J_1| < C_1 \int_{\mathbb{R}^3} \frac{1}{|x-y|^2}\, e^{-2|y|}\,dy \int_{|z|>|x|^\delta} e^{-2|z|}\,dz <$$

$$< C_1 \left[\left(\int_{|x-y|\le 1} + \int_{|x-y|>1}\right)\frac{1}{|x-y|^2} e^{-2|y|}\,dy\right] \int_{|z|>|x|^\delta} e^{-2|z|}\,dz < C_2 e^{-|x|^\delta},$$

where we use the summability of the function $1/|x-y|^2$ in the neighborhood of the point x. The other six integrals involve crossterms, for example,

$$J_2 = \iint \frac{1}{|x-y|}\frac{1}{|x-z|}\varphi_1^2(y)\varphi_2^2(z)\,dy\,dz = I_1 I_2,$$

where

$$I_2 = \int \frac{1}{|x-z|}\varphi_2^2(z)\,dz = \left(\int_{|x-z|\le 1} + \int_{|x-z|>1}\right)\frac{1}{|x-z|}\varphi_2^2(z)\,dz <$$

$$< C_3 e^{-2|x|^\delta} + \int \varphi_2^2(z)\,dz < C_3 e^{-2|x|^\delta} + C_4 \int_{|z|>|x|^\delta} e^{-2|z|}\,dz,$$

$$I_1 = \int \frac{1}{|x-y|}\varphi_1^2(y)\,dy = \left(\int_{|x-y|\le 1} + \int_{|x-y|>1}\right)\frac{1}{|x-y|}\varphi_1^2(y)\,dy <$$

$$< C_5 e^{-2|x|^\delta} + \int \varphi_1^2(y)\,dy < C_5 e^{-2|x|^\delta} + C_6 \int_{\mathbb{R}^3} e^{-2|z|}\,dz < C_7.$$

There are finitely many constants C_i; they can be easily estimated but are unimportant for our further aims. The other integrals are estimated similarly. The resulting estimates imply that

$$a_{12,12} = o\left(\frac{1}{r^6}\right).$$

We thus find similar estimates for $a_{22,22}$ and $a_{21,21}$. Finally, all these estimates and formulas (13) imply that there is a constant D_2 such that

$$c_2 > -\frac{D_2}{r^6}.$$

3.3.2. The upper estimate. We split the interval $(E_0+\epsilon_0,\infty)$ into the half-intervals

$$i_k=(a_k,a_{k+1}],\qquad k=1,2,\dots,\qquad a_1=E_0+\epsilon_0.$$

We can then write c_2 in the form

$$c_2=-\sum_k\int_{I_k}(\lambda-E_0)^{-1}\,d(VX_0,P_\lambda VX_0),\tag{15}$$

and each term in the sum is positive. Therefore, to find a lower estimate for this sum, it suffices to consider only the interval I_1, where a_2 is equal to the second eigenvalue of H_0. The second eigenvalue E_2 has the multiplicity eight, but in view of the same positivity, we can restrict ourself to one of the eigenvectors, for example, to $\Psi_1=\varphi(y)\varphi_1(z)$, where the function $\varphi(y)$ is defined in (7) and the function $\varphi_1(x)$ has the form (see [3])

$$\varphi_1(z)=\frac{1}{2\sqrt{2\pi}}e^{-|z|}\left(1-\frac{|z|}{x}\right).$$

We let P_{Ψ_1} denote the projection operator onto Ψ_1 and consider

$$(VX_0,P_{\Psi_1}VX_0)=(VX_0,(\Psi_1,VX_0)\Psi_1).$$

It can then be shown in the same way as above that for sufficiently large r, this expression admits the estimate

$$(VX_0,(\Psi_1,VX_0)\Psi_1)>\frac{C_{22}}{r^6}$$

with some constant $C_{22}>0$, whence it follows that

$$c_2<-\frac{D_1}{r^6},$$

where $B_2>0$.

3.4. The fourth statement in the theorem. The eigenvector $X=X_\beta$, which we do not assume to be normalized but do require that the condition

$$(X_0,X_\beta)=1\tag{16}$$

be satisfied, corresponds to the eigenvalue $E_\alpha(x)$, which is denoted by $E=E_\beta$ here. We recall that $X_0=\Psi_0=\varphi(y)\varphi(z)$ is a normalized eigenvector of H_0, i.e.,

$$H_0X_0=E_0X_0,\qquad \|X_0\|=1.$$

We introduce the projection operator P_0 onto X_0,

$$P_0F=(X_0,F)X_0.\tag{17}$$

We take the inner product of the obvious relation

$$(E_\beta-E_0)X_\beta=(H_0-E_0)X_\beta+\alpha VX_\beta$$

with X_0. By condition (16), this gives

$$\epsilon = \epsilon_\beta = E_\beta - E_0 = (X_0, \alpha V X_\beta). \tag{18}$$

In what follows, we assume that $\alpha = 1$, and we seek a "perturbed" eigenvector $X = X_\beta$ with the eigenvalue E_β for the Hamiltonian $H = H_0 + V$,

$$HX_\beta = E_\beta X_\beta. \tag{19}$$

It follows from the results in [6] on the convergence of the spectrum of H_β to the spectrum of H_0 as $\beta \to 0$ that for every sufficiently small neighborhood $O(E_0)$ of the point E_0, there exists β_0 such that for $\beta < \beta_0$, the intersection of the spectrum of $H(\alpha = 1, x)$ with $O(E_0)$ consists of the single eigenvalue E_β.

To estimate E, we now use the technique presented in [19]. As noted, ϵ can be taken sufficiently small. In this case, the operators $H_0 - E + cP_0$ and $H - E + cP_0$ have the same domain and have inverse operators for a fixed c and sufficiently small ϵ. Indeed, we introduce the spaces $P_0\mathbf{H}$ and $(1 - P_0)\mathbf{H}$. The operator $H_0 - E + cP_0$ acts as $H_0 - E$ on $(1 - P_0)\mathbf{H}$ and as multiplication by $c - \epsilon$ on X_0; therefore,

$$(H_0 - E + cP_0)^{-1} = (H_0 - E)^{-1}\left(1 - \frac{c}{c - \epsilon}P_0\right).$$

Hence, for sufficiently small β, the norm $\|(H_0 - E + cP_0)^{-1}\|$ is bounded by a constant independent of β. Therefore, the results in [6] again imply that the operator $(H - E + cP_0)^{-1}$ exists and that for sufficiently small β, its norm is bounded by a constant independent of β.

Consequently, we can write

$$\begin{aligned} H - E + cP_0 &= (H_0 - E + cP_0)(1 + (H_0 - E + cP_0)^{-1}V), \\ (H - E + cP_0)^{-1} &= (1 + (H_0 - E + cP_0)^{-1}V)^{-1}(H_0 - E + cP_0)^{-1}. \end{aligned} \tag{20}$$

Furthermore, the eigenvector X (by (17)) satisfies the equation

$$(H - E + cP_0)X = cX_0,$$

i.e.,

$$X = c(H - E + cP_0)^{-1}X_0.$$

Taking the scalar product of this equation by X_0, we obtain

$$1 = c(X_0, (H - E + cP_0)^{-1}X_0).$$

Using formula (20) and the relation

$$(H_0 - E + cP_0)^{-1}X_0 = (E_0 - E + c)^{-1}X_0,$$

we rewrite the equation for E in the form

$$1 = \frac{c}{c - E + E_0}(X_0, (1 + (H_0 - E + cP_0)^{-1}V)^{-1}X_0).$$

Multiplying by $c - E + E_0$ and subtracting the identity

$$c = c(X_0, (1 + (H_0 - E + c)^{-1}V)(1 + (H_0 - E + cP_0)^{-1}V)^{-1}X_0),$$

we finally obtain

$$\epsilon = \frac{c}{c-\epsilon}(VX_0, (1 + (H_0 - E_0 - \epsilon + cP_0)^{-1}V)^{-1}X_0). \tag{21}$$

We write

$$A = (H_0 - E_0 - \epsilon + cP_0)^{-1}.$$

Then

$$(1 + AV)^{-1} = 1 - (1 + AV)^{-1}AV,$$

and we can rewrite (21) as

$$\epsilon \doteq \frac{c}{c-\epsilon}(VX_0, (1 + AV)^{-1}X_0) = \frac{c}{c-\epsilon}[(VX_0, X_0) - (VX_0, (1 + AV)^{-1}AVX_0)]. \tag{22}$$

We can estimate the second term in the right-hand side in the same way as for c_2 if we note that (20) implies the boundedness of the norm of $(1 + AV)^{-1}A$,

$$|(VX_0, (1 + AV)^{-1}AVX_0)| \le \|VX_0\| \, \|(1 + AV)^{-1}A\| \, \|VX_0\| \le C(VX_0, VX_0).$$

The first term in the right-hand side of (18) decreases faster than any power of $1/r$. Hence, the resulting estimates give

$$E - E_0 = U(r) > -\frac{C}{r^6}$$

with some constant $C > 0$. The theorem is proved.

Remark. It seems that statements 3 and 4 in the theorem describe the exact asymptotic behavior of C/r^6. We see two possible approaches for proving this. The first approach is to take the whole spectrum, for which there are some explicit but rather cumbersome formulas, into account in expansion (15). The second approach is to use the Weinberg–van Winter cluster expansions for the resolvent or expansions similar to them.

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