

STABILITY THRESHOLDS OF QUANTUM SYSTEMS OF THREE CHARGED PARTICLES

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General diagram of stability thresholds (existence of bound states) for the ground and excited states, both symmetric and antisymmetric, is obtained in the mass-charge (m, Z) coordinate plane for a three-particle Coulomb system of XXY -type trions with zero total angular momentum. Variational optimization approaches with the use of Gaussian and exponential bases are proposed for high-precision three-particle calculations. A qualitative explanation of the stability diagram is given in the framework of the Born–Oppenheimer adiabatic approximation, by using simple approximating formulas for both symmetric and antisymmetric electronic energy curves.

1. Introduction

Three-particle systems like the molecular hydrogen ion H_2^+ , helium atom He , or the positronium ion Ps^- are among the most fundamental basic physical systems important for the understanding of specific three- and many-particle effects. Such systems are always considered as a benchmark for different approximate methods. Lately, a great progress was achieved in investigating many-particle quantum systems due to both the development of effective variational approaches to the analysis of the Schrödinger equation and the growth of computers performance (see [1, 2]). The general problem of stability of the ground state of a system of three charged particles was widely investigated for different mass and charge ratios [3, 4]. In the present work, the general stability diagrams (conditions of existence of the bound states) are presented for symmetric and antisymmetric energy levels of a system of three charged particles of two types, like symmetric trions XXY , with zero total angular momentum.

2. Formulation of the Main Result for Stability Thresholds

Consider a quantum system of three charged particles like an XXY trion with two identical particles of one

type (with masses $m_1 = m_2 = m$ and charges $Z_1 = Z_2 = 1$) and the third particle of another type with charge $Z_3 = -Z$ and mass $m_3 = M$ (we use the system of units with $e^2 = \hbar = 1$). Then the Hamiltonian takes the form

$$H = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m} + \frac{\mathbf{p}_3^2}{2M} + \frac{1}{r_{12}} - Z \left(\frac{1}{r_{13}} + \frac{1}{r_{23}} \right). \quad (1)$$

We consider the general problem of stability of XXY trions for different values of mass m and charge Z . It can be used for the description of different real systems, as well as for understanding the conditions of existence of different quasiparticle clusters in metals [5]. Three-particle energy levels $E_n(3; m, Z)$ (we consider here only zero full angular momentum and set $M = 1$ without loss of generality) depend only on the mass of equal particles m and the charge of the third particle Z . As it is usually done in the literature (see, e.g., [4, 6, 7]), we define that the system is stable (a bound state exists), if the energy of the n -th three-particle state is lower than the energy of the two-particle ground state:

$$E_n(3; m, Z) \leq E_0(2; m, Z), \quad (2)$$

where the two-particle threshold energy $E_0(2; m, Z) = -0.5mZ^2/(m+1)$. Condition (2) with the equality sign defines a certain line on the (m, Z) -plane for every three-particle level. This line separates the regions where the corresponding bound state of three particles exists (where $E_n(3) < E_0(2)$) and does not exist (where $E_n(3) > E_0(2)$ and the dissociation channel $(123) \rightarrow (23)+(1)$ is open). Below, we refer to these lines as the stability thresholds diagrams. Note that stability conditions for the ground state of the general problem of three different charged particles were investigated by many authors (particularly, [3–5]). The general results concerning a number of bound states for more complex Coulomb systems were obtained by Zhislin [6, 7].

It is well known that a three-particle system with Hamiltonian (1) for $Z > 1$ supports infinitely many

bound states for arbitrary values of m (the Kato theorem [8, 9]). Indeed, let us consider the simple polarizationless variational approximation and present the three-particle wavefunction as a product of the wavefunction of the ground state of the two-particle subsystem (2,3) and the wavefunction describing the motion of the first particle relative to the center-of-mass of this subsystem,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \approx \exp\left(-\sqrt{|E_0(2; m, Z)|} r_{23}\right) \psi(r), \quad (3)$$

where $\mathbf{r} \equiv \mathbf{r}_1 - (m\mathbf{r}_2 + \mathbf{r}_3)/(m + 1)$. Then the effective potential depending on the intercluster distance r has the form (in dimensionless units)

$$V_{\text{eff}}(r) = -\frac{(Z - 1)}{r} - \left(1 + \frac{1}{r}\right) \exp(-2r). \quad (4)$$

Since this is an upper estimate, we get asymptotically an attractive Coulomb potential and, consequently, the infinite spectrum for $Z > 1$. Examples of such three-particle systems are He, Li^+ , Be^{++} , ... Note that, for the effective long-range potential (4), there exist the infinite number of bound states for any value of the angular momentum. On the other hand, for $Z = 1$ and an arbitrary mass, at least one bound state always exists. This statement is known as the Hill theorem [10] and requires much more accurate estimates to be proved. Here, we consider energy levels for certain real physical three-particle systems (with $Z = 1$) and define stability diagrams for energy levels of problem (1) in a nontrivial case with $0 < Z \leq 1$.

We will study the three-particle problem spectra with Hamiltonian (1) within the variational Galerkin method [also referred to as the RRTBG (Rayleigh–Ritz–Timoshenko–Bubnov–Galerkin) method] with the use of Gaussian and exponential bases (see [11–13]). In this approach, the variational three-particle wavefunction is presented as a superposition of basis functions that depend only on three interparticle distances $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$:

$$\Psi(r_{12}, r_{13}, r_{23}) = \sum_{k=1}^K D_k \hat{S} \phi_k = \sum_{k=1}^K D_k \hat{S} \exp(-a_k r_{12}^n - b_k r_{13}^n - c_k r_{23}^n) \quad (5)$$

with a Gaussian ($n = 2$) or exponential ($n = 1$) basis. The symmetrization operator \hat{S} in (5) extracts symmetric (s) (singlet or para-states) and antisymmetric (a) (triplet or ortho-states) states with respect to the permutation of coordinates of identical particles 1 and 2.

The problem is then reduced to the solution of a system of linear algebraic equations for eigenvalues (the energy spectrum) and the determination of the eigenvector $\{D_k\}$, which allows us to reconstruct the wave function:

$$\sum_{m=1}^K D_m \{\langle \hat{S} \phi_k | \hat{H} - E | \hat{S} \phi_m \rangle\} = 0, \quad k = \overline{1, K}. \quad (6)$$

Another part of the problem is the optimization of the nonlinear parameters a_k, b_k , and c_k . The calculation method we use and the proposed original (both stochastic and deterministic) adaptive optimization schemes for the nonlinear parameters a_k, b_k , and c_k proved their high efficiency and allowed us to achieve relatively accurate or even high-precision results with a relatively small basis size.

Our main result, the diagrams of stability thresholds for quantum three-particle systems of the XXY -type, is presented on Fig. 1. Here, keeping all major visual regularities, the conditions for the existence of symmetric (s) and antisymmetric (a) bound states are qualitatively presented on the (m, Z) plane. For $Z < 0$, there are a repulsion between all particles and, consequently, no bound states. For $Z > 1$, the spectrum is always infinite. Both these regions are indicated in Fig. 1. The thresholds of stability are labeled as s_i for symmetric states and a_i for antisymmetric ones.

The quantum system of three charged particles described by (1) can be stable in the ground state for arbitrary mass m above the threshold line s_0 in the region $0 < Z \leq 1$ with respect to the $(23) + 1$ decomposition. Below this line, the system has no bound states. For all other symmetric and antisymmetric states, the system is bound only to the right and above the corresponding threshold lines in Fig. 1. Therefore, the low- m region of atom-like three-particle systems is very poor as for the bound states. In this region, when two light particles (two electrons) are in the attractive field of a heavy particle (Coulomb one-center problem), only the ground state exists for $Z = 1$ (e.g., atomic hydrogen ion H^-).

To perform calculations with high accuracy in the limit $m \ll 1$, it is reasonable to perform a scaling transformation $\mathbf{r}_i = \mathbf{x}_i/m$ in Hamiltonian (1). Then the identical particles will have masses equal to one, and the third particle will have effectively a very large mass (one also can set $m = 1$ and $M \neq 1$ in (1)). This allows us to perform more accurate calculations. Moreover, since we have a small parameter as a factor of the kinetic energy of the third particle and the operator \mathbf{p}_3^2 is always positive, the binding of three particles becomes less favorable with increase in m , and the curve s_0 somewhat

grows. We can claim that, due to the small factor $1/m$ (at large values of m) of the positive kinetic energy of two identical particles $(\mathbf{p}_1^2 + \mathbf{p}_2^2)/2m$ in (1), the threshold curve grows in this region with decrease in m . In the high- m region of molecular systems (Coulomb two-center problem), more and more excited states appear with increase in m (at first, only symmetric states, for higher m – both symmetric and antisymmetric ones). Note that we use the special expression $(1 - Z)^{-1}$ as a scale of the Y-axis in Fig. 1 to emphasize the $Z = 1$ case. We present the values corresponding to some reference systems in the upper part of the diagram for $Z \rightarrow 1 - 0$ and some examples of two-electron systems in its lower part.

To make the stability diagrams in Fig. 1 more demonstrative, Table 1 gives some characteristic points on the (m, Z) plane for the curve s_0 that are obtained with high-precision three-particle calculations. It is important that the stability threshold curve for the ground state $Z_0(m)$ has a maximum at some intermediate mass $m \cong 0.55$. Therefore, intermediate values of mass are least appropriate for the bound ground state formation. Both in the molecular limit $m \rightarrow \infty$ and in the atomic limit $m \rightarrow 0$, the stability curve $Z_0(m)$ reaches some minimal values. The symmetric ground state s_0 exists in the asymptotic limit $m \rightarrow \infty$ only for charges $Z \geq Z_{s(\text{crit})} = 0.810$. The same critical charge $Z_{s(\text{crit})}$ is characteristic of all excited symmetric states s_i . There-

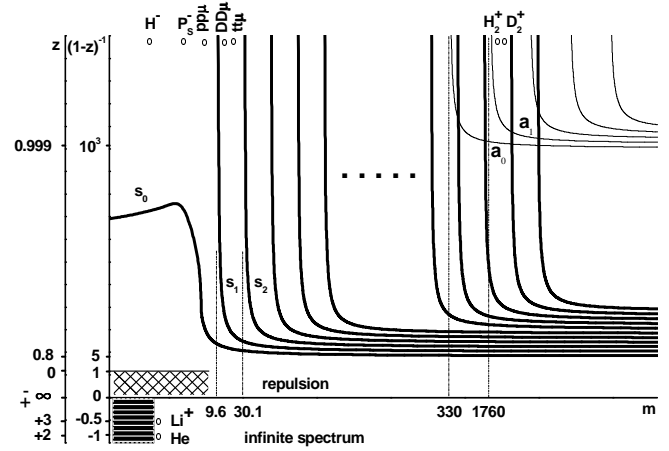


Fig. 1. Stability diagrams of energy levels of the system of three charged particles. Bold lines – symmetric states, thin lines – antisymmetric states

fore, with a sufficiently small charge $Z < Z_{s(\text{crit})}$, the system with Hamiltonian (1) has no symmetric bound states for any masses (universality). Excited symmetric states can exist for $Z \leq 1$ only in the molecular region with sufficiently large masses $m \geq m_{n(\text{crit})}^{(s)}$ (Table 2, second column), and $m_{n(\text{crit})}^{(s)}$ are defined by condition (2) for $Z = 1 - 0$. The dependence of the critical mass $m_{n(\text{crit})}^{(s)}$ on the bound state number can be approximately presented for any value of n as

$$m_{n(\text{crit})}^{(s)} \approx 5n(n + 1). \tag{7}$$

Respectively, the values of critical masses for antisymmetric states are presented in Table 3 (second column): antisymmetric states can exist only in the molecular region.

The values of critical masses from Table 3 conform the approximate expression

$$m_{n(\text{crit})}^{(a)} \approx 715n(n + 1) + 330. \tag{8}$$

In the asymptotic case $m \rightarrow \infty$, all thresholds in Fig. 1 for antisymmetric states lie above the asymptotic value of critical charge $Z_{a(\text{crit})} = 0.9997$. Namely, for $Z < Z_{a(\text{crit})}$ and any masses, the system with Hamiltonian (1) has no bound antisymmetric states (universality).

3. Adiabatic Born–Oppenheimer Approximation

To confirm our main conclusions about the stability diagrams in Fig. 1, we use a simplified variational adiabatic Born–Oppenheimer approximation (BO) (see [14])

Table 1. Ground state s_0

m	Z_0	m	Z_0
0	0.911028	2.0	0.912062
0.001	0.911106	5.0	0.89058
0.01	0.91177	10.0	0.87273
0.1	0.91702	100.0	0.8414
0.2	0.92061	10^3	0.8170
0.55	0.924271	10^4	0.8113
1.0	0.921802	10^6	0.81009
1.5	0.91700	10^8	0.81007

Table 2. Critical values of mass $m_{n(\text{crit})}^{(s)}$ for symmetric states

n	$m_{n(\text{crit})}^{(s)}$ 3-part. calc.	$m_{n(\text{crit})}^{(s)}$ approx. BO
0	0.	1.464
1	9.53	11.19
2	29.66	31.17
3	59.68	60.87
4	99.76	100.50
5	149.9	148.46

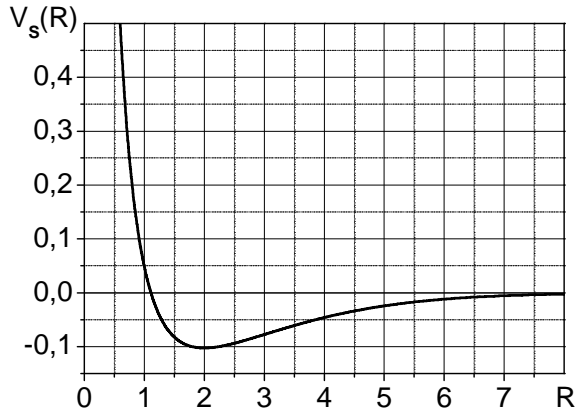


Fig. 2. Symmetric electronic term from (10). $V_s(R) = U_s(R) + 0.5 + 1/R$

in the region of large values of m , when the third particle can be considered as one moving in the external field of two Coulomb centers. We can rewrite the Schrödinger equation with Hamiltonian (1) in the center-of-mass coordinate system:

$$\left\{ -\frac{1}{m + \frac{1}{2}} \Delta_{\mathbf{R}} - \frac{1}{2} \Delta_{\mathbf{r}} + \frac{1}{ZR} - \frac{1}{|\mathbf{r} - \frac{\mathbf{R}}{2}|} - \frac{1}{|\mathbf{r} + \frac{\mathbf{R}}{2}|} \right\} \Psi(\mathbf{r}, \mathbf{R}) = \mathcal{E} \Psi(\mathbf{r}, \mathbf{R}), \quad (9)$$

where the energy \mathcal{E} is related to the eigenvalue of Hamiltonian (1): $\mathcal{E} = EZ^{-2}(1 + 1/2m)$. Here, for convenience, a new scale and the relative coordinates are introduced: $\mathbf{R} = (\mathbf{r}_1 - \mathbf{r}_2)Z(1 + 1/2m)^{-1}$ and $\mathbf{r} = (\mathbf{r}_3 - (\mathbf{r}_1 + \mathbf{r}_2)/2)Z(1 + 1/2m)^{-1}$. In the limit $m \rightarrow \infty$, (9) is reduced to the standard problem of an electron in the field of two Coulomb attraction centers (fast motion along \mathbf{r} coordinate and slow movement along \mathbf{R}). Then there is a separation of electronic and vibrational spectra (see, e.g., [14]) — $\Psi(\mathbf{r}, \mathbf{R}) \approx \Phi(\mathbf{r}, R)\chi(R)$. For the electron dynamics, one can obtain

$$\left\{ -\frac{1}{2} \Delta_{\mathbf{r}} - \frac{1}{|\mathbf{r} - \frac{\mathbf{R}}{2}|} - \frac{1}{|\mathbf{r} + \frac{\mathbf{R}}{2}|} \right\} \Phi(\mathbf{r}; R) = U(R)\Phi(\mathbf{r}; R). \quad (10)$$

We note that the eigenvalues of this equation $U_{(s,a)}(R)$ depending on the distance between nuclei define symmetric and antisymmetric electronic terms (with respect

to the permutation of nuclei coordinates) $1s_\sigma$ and $2p_\sigma$). These electronic terms were obtained by the numerical investigation of Eq. (10) and are presented in Figs. 2 and 3 shifted by the asymptotic value $-1/2 - 1/R$. We should like to emphasize the important result that Eq. (10), as well as its solutions, are independent of the value of charge. This allows us to use, for arbitrary Z , the standard consideration of a molecular hydrogen ion H_2^+ ($Z = 1$). Note that the symmetric electronic term (Fig. 2) contains a relatively deep attractive well ($\min V_s(R) = -0.102635$ at $R_{\min} = 1.99719$), which results in more and more symmetric vibrational bound states in (9) with increase in m .

It is less known and was first indicated in [15] that the antisymmetric electronic term (Fig. 3) also contains some shallow negative minimum at relatively large distances ($\min V_a(R) = -0.0000608$ at $R_{\min} = 12.55$). This minimum also rises a growing series of antisymmetric vibrational bound states of problem (9).

The total energy in (9) in the adiabatic variational approximation is defined by the equation for slow vibrational levels

$$\left\{ -\frac{1}{m + \frac{1}{2}} \Delta_{\mathbf{R}} + \frac{(1/Z - 1)}{R} + V_{(s,a)}(R) \right\} \psi_{n(s,a)}(R) = \mathcal{E}_{n(s,a)} \psi_{n(s,a)}(R). \quad (11)$$

To investigate efficiently (with minimal numerical effort) the vibrational spectra of Eq. (11) and to provide a general possibility to analyze the system with arbitrary m and Z , we will obtain a convenient approximate analytical representation of electronic terms. We take into account all known polynomial and exponential asymptotic expressions at large distances between nuclei $R \gg 1$ (see [14]):

$$V_{(s,a)}(R) = Q_{as.} = Q_1(R) \mp Q_2(R), \quad (12)$$

where

$$Q_1(R) = -\frac{9}{4R^4} - \frac{8}{R^6} - \frac{213}{4R^7} - \frac{7755}{64R^8} - \frac{1773}{2R^9} -$$

Table 3. Critical values of mass $m_{n(\text{crit})}^{(a)}$ for antisymmetric states

n	$m_{n(\text{crit})}^{(a)}$, 3-part. calc.	$m_{n(\text{crit})}^{(a)}$, approx. LH	$m_{n(\text{crit})}^{(a)}$, approx. BO
0	333.1	344.	339.
1	1760.	1900.	1838.
2	4600.	4790.	4596.
3	8940.	8945.	8407.
4	17500.	14290.	13471

$$-\frac{86049}{16R^{10}} + O(1/R^{11}), \tag{13}$$

$$Q_2(R) = 2Re^{-1-R} \left[1 + \frac{1}{2R} - \frac{25}{8R^2} - \frac{131}{48R^3} - \frac{3923}{384R^4} - \frac{145399}{3840R^5} - \frac{5219189}{46080R^6} - \frac{509102915}{645120R^7} - \frac{37749539911}{10321920R^8} + O(1/R^9) \right]. \tag{14}$$

In (13), the main asymptotic term corresponds to the polarization potential of a hydrogen atom, while the main exponential asymptotic term in (14) is the well-known Landau–Herring anomalous additional term [2, 14, 16, 17]. In (12), we need to choose the plus and minus signs for the symmetric and antisymmetric electronic terms, respectively. This asymptotic formula is already applicable at $R \approx 10.0$ for the symmetric electronic term, and at $R \approx 30.0$ for the antisymmetric one. The behavior of electronic terms at small distances $R < 0.1$ can be approximated by the pure Coulomb repulsion $1/R$.

Approximating expressions for the symmetric electronic term can be presented in different regions of R in the next forms: I – $1/R$ asymptotics at $R < 0.1$; IV – (12)–(14) at $R > 10.0$; and two segments in the intermediate region: II – $(0.1 \leq R < 2.5)$ and III – $(2.5 \leq R \leq 10.0)$. In segment II, we use the approximating function in the form

$$V_s(R) = \frac{1}{R} \sum_{k=0}^{10} a_k R^k \tag{15}$$

with parameters presented in the second column of Table 4.

Table 4. Parameters of approximating function (15) and (16) for the symmetric electronic term

k	$a_k(\text{II})$	$b_k(\text{III})$
0	1.0006265	0.658208
1	-1.5157411	6.879508
2	0.1537749	-51.718667
3	1.9167176	191.225093
4	-3.5973973	-442.496156
5	3.8464339	695.083378
6	-2.6905681	-770.696778
7	1.2404386	611.758946
8	-0.362321	-346.003729
9	6.0660188×10^{-2}	136.160477
10	$-4.4280974 \times 10^{-3}$	-35.415915
11		5.470783
12		-0.379851

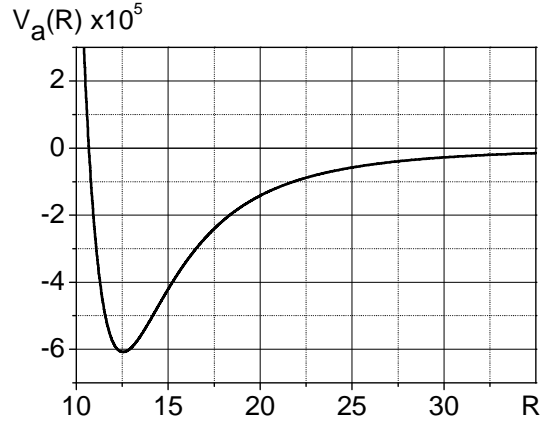


Fig. 3. Antisymmetric electronic term from (10). $V_a(R) = U_a(R) + 0.5 + 1/R$

In segment III $(2.5 \leq R \leq 10.0)$, we use the approximating function in the form

$$V_s(R) = Q_{\text{as.}}(R) \sum_{k=0}^{12} b_k (R - 2)^{-k}, \tag{16}$$

where the function $Q_{\text{as.}}(R)$ is taken from (12) with a minus sign, and the parameters b_k are presented in the third column of Table 4. The relative error of the symmetric electronic term approximated by the above functions is not higher than 4×10^{-3} for all values of R .

The approximation of the antisymmetric electronic term is a slightly more complex problem. Apart of asymptotic regions I ($R < 0.1$) and V ($R > 30.0$), where the corresponding asymptotic expressions can be used, we split the intermediate region into three segments: II $(0.1 \leq R \leq 4)$, III $(4 < R < 12)$, and IV $(12 \leq R \leq 30)$. In segment II, the following approximating function is used:

$$V_a(R) = \frac{c_0}{R} + \sum_{k=1}^9 c_k \left(\frac{R}{4}\right)^{k+1} \tag{17}$$

with parameters presented in the second column of Table 5. In segment III, the electronic energy curve is approximated by the expression

$$V_a(R) = \frac{d_0}{R^4} + e^{-R} \left(d_1 \left(\frac{R}{4}\right) + \sum_{k=2}^8 d_k \left(\frac{4}{R}\right)^{k-2} \right) \tag{18}$$

with parameters presented in the third column of Table 5. Note that the first term in (18) is very close to the polarization term $-2.25/R^4$ mentioned above. In segment IV, the electronic energy curve is approximated

by the expression

$$V_a(R) = Q_{as.}(R) \sum_{k=0}^4 f_k \left(\frac{12}{R} \right)^k . \tag{19}$$

The relative error of the symmetric electronic term approximated by the above functions is not higher than 7.6×10^{-4} . Now we can use the obtained approximating expressions and define the general parameters of stability diagrams using the adiabatic approximation (11). At first, we note that, in the adiabatic BO approximation, the symmetric states are stable for $Z > Z_{s(crit)}$, and the antisymmetric states are stable for $Z > Z_{a(crit)}$. These asymptotic critical values can be defined from Eq. (11) with the use of the condition

$$\min_R \left\{ \frac{1-Z}{ZR} + V(R) \right\} = 0 , \tag{20}$$

which gives

$$Z_{crit} = (1 - R_m V(R_m))^{-1} \tag{21}$$

and

$$V(R_m) = R_m V'(R_m) . \tag{22}$$

Relations (21), (22) result in the following asymptotic critical charges (horizontal asymptotes in Fig. 1):

$$Z_{s(crit)} = 0.8086 , \quad Z_{a(crit)} = 0.99922 . \tag{23}$$

In the limit $m \rightarrow \infty$, these are the most exact values for the full tree-particle problem as well. We see that the values obtained above by variational three-particle calculations (with the Gaussian basis with 300–500 components or a little smaller exponential basis) are less accurate. In the third column of Table 2, we present the critical masses in the BO approximation. The corresponding

Table 5. Parameters of approximating functions (17)–(19) for the antisymmetric electronic term

k	c_k (II)	d_k (III)	f_k (IV)
0	1.000012	-2.29795	0.98489
1	-1.217195	0.55964	0.0948819
2	3.67718	20.8858	-0.2203
3	-37.46265	-76.6861	0.21973
4	179.2744	150.059	-0.0810585
5	-424.6429	-171.083	
6	570.7409	117.126	
7	-447.6394	-44.7849	
8	192.0168	7.38616	
9	-34.94273		

bound states are exist only above these values. We emphasize that the adiabatic BO approximation provides an upper variational upper estimate for all three-particle levels, stability thresholds, and critical masses $m_{n(crit)}^{(s)}$. Moreover, with increase in the mass m , the accuracy of the BO approximation becomes higher. In Table 2, we can see that the BO approximation gives a lower result, starting from the fifth excited level. This means that, for these values of masses, the BO approximation is already more accurate than the proposed three-particle variational scheme. To control the accuracy of three-particle calculations, we performed them in both Gaussian and exponential bases. Usually, we need more Gaussians than exponents to achieve the same accuracy. But, on the whole, the calculations are more stable and the matrices are well-conditioned with a Gaussian basis (for a basis size up to 400–600 functions). Therefore, for highly-excited levels, it is better to analyze the stability thresholds within the BO approximation. For very small values of masses m and $Z < 1$, a three-particle system has no bound states in the BO approximation (the system of three charged particles is absolutely unstable, and the conditions of the Hill theorem are not satisfied), and the diagrams of stability thresholds are similar for all symmetric levels of the system.

We note that the approximate formula (7) quadratic by the level number n for highly excited levels (high values of n) can be explained in the “quasiclassical” approximation (if $1/m \rightarrow 0$ and fixed, then $\sqrt{1/m}(n+1/2)$ can be treated similarly to $\hbar(n+1/2)$) of the adiabatic equation (11). As a result, we get

$$m_{crit} + \frac{1}{2} \approx \left(\frac{\pi}{J} \right)^2 \left(n + \frac{1}{2} \right)^2 , \tag{24}$$

where the quasiclassical integral

$$J = \int_{R_0}^{\infty} dR \sqrt{-V(R)} , \tag{25}$$

and the integration is performed over the region of negative values of $V(R)$ (for symmetric states – $R_{0(s)} = 1.10$, for antisymmetric – $R_{0(a)} = 10.69$). Then the coefficient $(\pi/J)^2$ (exact asymptotics for highly excited states) for symmetric states is equal to 4.72, which is sufficiently close to the empiric value ≈ 5.0 in (7). For antisymmetric states, the asymptotic coefficient is ≈ 585 , which is also not far from relation (8).

We can expect that, with a further increase in the mass, the BO approximation becomes more accurate

than our three-particle calculations also for lower levels. Let us compare the critical values of masses for antisymmetric states (Table 3) obtained from different schemes of the BO approximation and from three-particle calculations. In the third column, the values of $m_{n(\text{crit})}^{(a)}$ are presented in the Landau–Herring approximation [16, 17] using only leading terms in asymptotic expressions, when the polarization potential of a hydrogen atom $-9/4R^2$ is taken into account, and $V_{a(\text{LH})} \approx -9/4R^2 + 2Re^{-R-1}$. The fourth column contains the critical masses obtained with the asymptotic BO approximation, when all known asymptotic terms are included (12). Note that the simplest Landau–Herring approximation for the antisymmetric electronic term gives qualitatively correct values of critical masses, and probably, that is an upper estimate of critical masses. At the same time, starting from the second excited level, the results of the asymptotic BO approximation are accurate enough and better than those of direct three-particle calculations.

4. Spectra of Some Realistic Three-particle Systems

The diagrams of stability thresholds (Fig. 1) allow one, by the value of mass m of two identical particles and charge Z of the third particle, to determine whether the system is stable and the number of its bound states. In perspective, it is possible to build 3-dimensional pictures of energy surfaces for the lowest levels depending on m and Z .

1. Atomic hydrogen ion H^- (pee) with $Z = 1$, $m = 1$, and $M = m_p/m_e = 1836.152701$ has only one bound state symmetric with respect to the permutation of electrons. Its energy calculated on 200 Gaussian basis functions is (in atomic units)

$$E_{s_0}(\text{H}^-) = -0.5274458. \quad (26)$$

The calculation with an exponential basis of 140 components gives -0.527445881 . The experimental value of the energy of an atomic hydrogen ion agrees with (26) in four first digits: -0.52743 ± 0.00002 a.u. By the way, in the case of a fixed center ($m_p \rightarrow \infty$), the energy of H^- ion obtained with 200 Gaussian functions is -0.5277508 , while the result with 180 exponent functions is slightly better: -0.5277510165 . This result corresponds to the best calculations of other authors with basis sizes around 850 components [1]. Mean-square distances of particles from the center of mass are (in atomic units)

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{R})^2\rangle} = 3.445, \quad \sqrt{\langle(\mathbf{r}_3 - \mathbf{R})^2\rangle} = 0.00257. \quad (27)$$

Thus, a proton is situated almost at the center-of-mass of the whole system. Moreover, the geometric structure of H^- forms an isosceles triangle with distances between particles

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_3)^2\rangle} = 3.447, \quad \sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_2)^2\rangle} = 5.014. \quad (28)$$

Other peculiarities of structure functions, like density distributions and pair correlation functions, are the subject of the further investigation.

2. Positronium ion Ps^- ($e^-e^-e^+$, $am = M = Z = 1$) has also only one bound state with zero angular momentum that is symmetric with respect to the permutation of electrons and with energy (in a.u.)

$$E_{s_0}(\text{Ps}^-) = -0.26200507012, \quad (29)$$

which agrees with the experimental value in five first digits. This result was obtained with 185 exponential basis functions (a more accurate result, -0.262005070226 , was obtained with 600 Gaussian functions in [2]). Note that, for the considered system, the calculations with exponential basis are more accurate and stable enough. The corresponding mean-square distances of particles from the center of masses are (in a.u.):

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{R})^2\rangle} = 5.10, \quad \sqrt{\langle(\mathbf{r}_3 - \mathbf{R})^2\rangle} = 3.34. \quad (30)$$

Thus, a positron is attracted by electrons and, therefore, situated somewhat closer to the center of masses. The mean-square distances between particles are:

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_3)^2\rangle} = 6.95, \quad \sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_2)^2\rangle} = 9.64. \quad (31)$$

3. Much richer data (see, e.g., [18–20]) are available for molecular hydrogen ion H_2^+ (ppe). For this system with $Z = 1$ and $m = 1836.152701$, the energy of two-body dissociation

$$E_0(2) = -\frac{m}{2(m+1)} = -0.499727839716.$$

It is clear from the diagram of stability in Fig. 1 that the molecular hydrogen ion has a large number of symmetric bound states. The number of symmetric levels of a molecular hydrogen ion estimated from the asymptotic formula (7) is around 20 or 21. From the special high-precision investigation performed in [19], it is known that the overall number of symmetric levels is 20. With 500 Gaussian functions, when our variational calculations schemes can still give a stable controlled result, we obtain that the ground state energy of H_2^+

$$E_0 = -0.59713752, \quad (32)$$

while the best result available in the literature is $-0.5971390631239(5)$ [21]. The experimental value of the dissociation energy of H_2^+ ion agrees with these values up to the fifth digit. As seen, our calculations give an error in the sixth digit with a relatively small basis size. The mean-square distances from the center of masses for the ground symmetric state of H_2^+ ion are

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{R})^2\rangle} = 1.04, \quad \sqrt{\langle(\mathbf{r}_3 - \mathbf{R})^2\rangle} = 1.57, \quad (33)$$

and mean-square distances between particles are

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_2)^2\rangle} = 2.077, \quad \sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_3)^2\rangle} = 1.887. \quad (34)$$

For the energy of the first excited level, we obtained the following result with 400 Gaussian functions:

$$E_1 = -0.587101, \quad (35)$$

while the best result in the literature is $-0.5871556792136(5)$ [21]. Therefore, our result obtained with stable schemes on a 32-bit PC with double-precision arithmetic is correct in four first digits. We were able to obtain only 12 symmetric levels of a molecular hydrogen ion with our direct three-particle calculations, while the overall number of levels obtained in ultra-precision calculations is 20.

We now compare the spectrum of H_2^+ calculated in the full three-particle approach and in the BO approximation. In Table 6, we present the dissociation energies (the difference between the ground state energy of the hydrogen ion and the energy of the three-particle system, $E_0(2) - E_n(3)$) calculated in the adiabatic BO approximation (second column) and by direct three-particle calculations (third column). In the fourth column, the best published results are collected. It is clearly seen that, for large masses and excited levels, the BO approximation is considerably more accurate and definitely simpler as compared with resource-intensive direct three-particle calculations. Even for the ground state, the BO approximation gives a sufficiently high accuracy (four significant digits agree with the best result). We also note that this comparison of energy spectra confirms the sufficient accuracy of the approximating formulas from Section 3.

Recently, it was proved by ultra-precision three-particle calculations in [2, 20] that the molecular hydrogen ion has two antisymmetric bound energy levels. This fact was first ascertained in the adiabatic approximation in [15]. We confirm the existence of two antisymmetric states in H_2^+ ion within the BO approximation:

$$E_0 = -0.4997435, \quad E_1 = -0.4997278407. \quad (36)$$

The corresponding dissociation energies ($D \equiv E_0(2) - E_n(3)$) are

$$D_0 = 1.5634637 \times 10^{-5}, \quad D_1 = 0.9888288 \times 10^{-9}$$

which are close enough to the reference results from [2] (see the last column in Table 6). In our three-particle calculations with the exponential basis of 430 components, we obtained both antisymmetric states (third column in Table 6). With the Gaussian basis of 560 functions, we were able to obtain only the lowest antisymmetric level of H_2^+ with the energy $E_0 = -0.499743405$ that differs only in the 7-th digit from the result in (36). The mean-square distances from the center of masses in H_2^+ in the lowest antisymmetric state are:

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{R})^2\rangle} = 8.82, \quad \sqrt{\langle(\mathbf{r}_3 - \mathbf{R})^2\rangle} = 8.97. \quad (37)$$

The mean-square distances between particles:

$$\sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_2)^2\rangle} = 17.636, \quad \sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_3)^2\rangle} = 12.579. \quad (38)$$

The exponential basis is substantially better than the Gaussian one, because the former can appropriately reproduce the asymptotic behavior of a wavefunction. But it is mostly impossible to perform high-precision calculations with a large number of exponential basis functions because of the instability of numerical calculations of the energy eigenvalues.

Concerning the other systems with hydrogen isotopes, we note that 27 symmetric levels are expected for ion D_2^+ (relative mass of a deuteron is 3670.483014) (7), which conforms the results of other authors. But there are only two antisymmetric levels in this system, similarly to H_2^+ , which is seen from Table 3. For a molecular tritium ion

Table 6. Dissociation energies of H_2^+

n	BO (appr. curve)	Our 3-part. calc.	Other authors
Symmetric states			
0	0.097397	0.09740898	0.097416 [21]
1	0.08742	0.08737	0.087428 [21]
2	0.078005	0.07766	0.078020 [2]
3	0.069152	0.0678	0.069172 [2]
4	0.060854	0.0559	0.060881230 [19]
5	0.053081	0.0449	0.053112692 [19]
6	0.045831	0.032	0.045864533 [19]
7	0.039096	0.018	0.039129221 [19]
Antisymmetric states			
0	1.56346×10^{-5}	1.554×10^{-5}	1.56625×10^{-5} [2]
1	0.9888×10^{-9}	0.83×10^{-9}	1.085045×10^{-9} [2]

T_2^+ (relative mass of the triton is 5496.918), 33 symmetric levels are expected (7), and 3 antisymmetric levels can be seen in Table 3. It is now evident (according to the diagrams in Fig. 1) that the binding is impossible for such three-particle systems as molecular ions with one electron like He_2^{+++} and heavier, because the value of Z in (1) is too small ($Z \leq 0.5$).

4. For a full description of the stability diagram in Fig. 1 for any charge Z , we need to make some remarks concerning the region $Z > 1$ and, in the first turn, two-electron systems. For a helium atom ($Z = 2$, $m = 1$ and $M = 7294.2995$ (1)), it is well known (see, e.g., [22]) that, in both symmetric (para-helium) and antisymmetric (ortho-helium) states with respect to spatial variables, there are the infinite series of levels lower than the dissociation threshold, also known as the Grotrian diagram. This result has clear explanation in the one-particle shell approximation, using perturbation theory in a repulsive electron-electron potential (see [23–25]), as well as direct variational estimates [26].

The results of direct three-particle calculations of the lowest energy levels of the helium atom are presented in Table 7. These calculations were performed with the exponential basis (presented values are obtained with a basis size of about 130 functions, when the convergence is reached), which gives a much better accuracy for this problem than the Gaussian basis. We indicate some details of the structure of energy spectra of two-electron systems. The infinite series of symmetric and antisymmetric energy levels are alternating, which can be explained by taking a proper account of exchange effects between two electrons within perturbation theory in the electron-electron repulsive potential. This consideration is most appropriate for large Z , because the potential between electrons is Z times smaller than the attraction to a nucleus, and electron-electron correlations are small. Moreover, the alternating behavior of levels with different symmetries exists for all values of mass, both in the atomic and molecular regions, and for all values of charge

Table 7. Energy spectrum of a helium atom: n – level number, (s) – symmetric states, (a) – antisymmetric states

n	a	a
0	-2.90330444	-2.17493011
1	-2.14567849	-2.06840517
2	-2.0609890	-2.03623268
3	-2.03330771	-2.022344
4	-2.0208997	-2.015100
5	-2.0142867	-2.010852
6	-2.0103483	-2.008109

Z more than 1. In the one-particle approximation, the exchange energy has different signs for the singlet and triplet states, and the levels from one shell are split in such a way that the triplet states (antisymmetric with respect to spatial variables) are always situated lower than the singlet ones (symmetric with respect to spatial variables). Finally, all described properties are intrinsic to all other two-electron ions like Li^+ , Be^{+2} , C^{+4} , O^{+6} .

5. Conclusions

To conclude, we note that the diagrams of stability with zero total angular momentum which are constructed in the present work allow one to associate every real physical system (of the XXY-type) with a point on the diagram (Fig. 1). The location of this point will immediately show the number of symmetric and antisymmetric bound states in the system. The diagrams of stability thresholds are obtained by high-precision variational calculations of the three-particle problem of charged particles of two types and confirmed within the adiabatic Born–Oppenheimer approximation. Moreover, we present two lowest electronic energy terms with easy-to-use approximating formulas, which allows one to investigate the vibrational spectra and other properties of a system of three charged particles with a minimal effort.

Our investigation revealed a nonmonotonic dependence of the binding conditions on the masses of two identical particles: the situation where all masses are of the same order is the least suitable for the existence of a bound state (e.g., positronium ion Ps^-). At the same time, the best conditions for binding are in the molecular region, when a light electron moves in the field of two heavy Coulomb centers and binds them together. Moreover, for the binding of a three-particle system, it is necessary that the relative charge of the third particle be not much less than 1 (two doubly charged nuclei already cannot be bound by an electron).

A separate attention is required for the investigation of structure peculiarities of real three-particle systems and the consideration of a rotational motion and relativistic effects for an electron in the two-center problem. These questions will be considered elsewhere.

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ПОРОГИ СТАБІЛЬНОСТІ КВАНТОВИХ СИСТЕМ
ТРЬОХ ЗАРЯДЖЕНИХ ЧАСТИНОК

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Резюме

Отримано загальну діаграму порогів стабільності (наявності зв'язаних станів) для основного і збуджених станів як симетричних, так і антисиметричних, на площині маса-заряд (m, Z) для тричастинкових кулонівських систем типу тріонів XXY з нульовим кутовим моментом. Для прецизійних тричастинкових чисельних розрахунків запропоновано варіаційні оптимізаційні підходи з використанням гаусоїдних та експоненціальних базисів. Дано якісне пояснення діаграм стабільності в рамках адиабатичного наближення Борна-Оппенгайма з використанням зручних апроксимаційних формул для симетричного і антисиметричного електронних термів.