Critical charge of one electron and five/six-charged centers system

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Coulomb system of one electron and five/six infinitely massive centers of charge $Z$: $(5Z, e)$ and $(6Z, e)$ is considered. Critical charges and optimal geometrical configurations are found. It is shown that the domain of stability for $(5Z, e)$ is $0 < Z \leq Z_{cr}^{(5Z,e)} = 0.350$ with optimal geometrical configuration is given by dipyramid (equilateral triangle base) circumscribed in prolate spheroid. For $(6Z, e)$ the stability is $0 < Z \leq Z_{cr}^{(6Z,e)} = 0.335$ with optimal geometrical configuration given by octahedron (square base) circumscribed in oblate spheroid. For both systems it is obtained an indication that total energy at $Z = Z_{cr}$ has a square-root branch point singularity with exponent $3/2$.

I. INTRODUCTION

In recent years it has been discovered that bound states for one-electron system with three-four protons exist in Nature in presence of a strong magnetic fields [1]. In particular, for molecular ion $H_3^+$ it is shown that geometrical configurations change depending on the field strength, being an equilateral triangle for $10^8 < B < 10^{11}$ G and linear for $10^{10} < B < 4.414^{13}$ G. Systems with more than three protons also exist in presence of such a strong fields but the only linear configurations parallel to the field seems to be the optimal, though it might exist other geometrical configuration in such circumstances but so far have not been studied. In a very naive way of thinking a clue to find others configurations is when proton is considered to have non-integer charge. Although the physics behind of this two phenomena are totally different is possible that for a given field strength there will be a preferred direction for which a geometrical configuration, different from linear, might be realized. In work [2] on one-electron systems with charged centers $(nZ, e)$, $n = 2, 3, 4$, it has been shown the existence of bound states for positive charges less that a certain critical one, $Z \leq Z_{cr}$, with non-linear optimal geometrical configuration.

Restriction to values of charges in classical electrodynamics and not even in more advanced theories such as the theory of atomic-molecular physics do not appear, it is only in elementary particle physics [3, 4] where justification of existence of integer charge appears. In classical electrostatics where it is known that the stable configurations of point charges are absent (the Earnshaw’s theorem), with zero charge as a singular point where the nature of interaction changes from repulsion to attraction. Usually, at a singular charge the whole or some part of the potential vanishes. This behavior is not exclusive of classical physics, it can be found in non-relativistic quantum electrodynamics where these singular charges continue to exist, however, a new phenomenon occurs - there are some critical charges which separate the domain of the existence of the bound states from the domain of non-existence, although the nature of potential remains unchanged. In some cases a system gets bound at a critical charge with polynomial-decaying eigenfunctions at large distances unlike standard exponentially-decaying eigenfunctions [5]. The well-known examples where such a phenomenon, of existence to non-existence, occurs are the square-well of finite depth, the Pöschl-Teller potential and the Yukawa potential. About Coulomb molecular systems, there are some works related with molecular ion $H_3^+$ with non-integer charge [6, 7]. For more than two charged centers and one electron the first study was presented in [2] for $n = 2, 3, 4$: $(2Z, e)$, $(3Z, e)$ and $(4Z, e)$, where critical charges were calculated and the optimal geometric configurations were found to correspond to Platonic solids; line for $(2Z, e)$, equilateral triangle for $(3Z, e)$ and a regular tetrahedron for $(4Z, e)$. For all studied systems, both atomic and molecular, the total energy has a square-root branch point with exponent $3/2$ at $Z = Z_{cr}$.

This work can be considered as a continuation of [2] considering five and six infinitely massive centers of the same charge $Z$ and one electron. One of the goals is to find the possible optimal geometrical configuration for which the system is realized. Another goal is to localize the domain(s) in $Z$ where the system is bound focusing on finding the critical charges $Z_{cr}$ which separate the domains of existence/non-existence of bound state.

The study is made in framework of the non-relativistic quantum mechanics. Atomic units ($\hbar = e = m_e = 1$) are used throughout, but energies are given in Rydbergs.

II. GENERAL CONSIDERATIONS

Let us consider the Coulomb molecular system which consisting in $n$ fixed charges $Z$ and one electron, $(nZ, e)$. The Hamiltonian which describes this system is written
in the following way

$$\mathcal{H} = -\frac{1}{2} \Delta + \sum_{i<j} \frac{Z^2}{R_{ij}} - \sum_{i=1}^{n} \frac{Z}{r_i}, \quad (1)$$

in a.u., where $R_{ij}$ is the distance between charge centers $i$ and $j$, $r_i$ is the distance from the electron to $i$th charge center.

From a physical point of view, it is clear that such a system is not bound for both large positive and for negative $Z$ values. However, it has to be bound at small $Z > 0$. It is clear that there must exists a critical charge which separates the domain of existence from non-existence of the bound state; one such a critical charge is at $Z = 0$, another one is at some certain finite $Z$, $Z = Z_{cr}$, which not represent any type of singularity of operator (1).

In order to calculate the total energy $E(Z)$ the variational method is used. We employ the physics-inspired trial functions. The choice of the trial function is based on arguments of physical relevance, e.g. the trial function should support the symmetries of the system, has to reproduce the Coulomb singularities and the asymptotic behavior at large distances adequately (for more details see [1, 8–10]).

### III. SYSTEM $(5Z, e)$

Let us consider five fixed charges $Z$ and one electron. There are an infinite number of different configuration for this system but only one that is optimal. It is impossible to study all different configurations but it is a good guess to consider the most symmetric ones. Three particular configurations were studied: pentagon, square pyramid and triangular dipyramid. For the pentagon configuration protons were located on the $x - y$ plane with origin in the centroid, and $L$ the distance between two adjacent protons. In square pyramid configuration four protons were placed on the corners of a square of side $L$, defining the $x - y$ plane with its sides parallel to the axes, the fifth proton is placed on the $z$, axis perpendicular to the square. Finally the triangular dipyramid configuration is given by three centers forming an equilateral triangle of side $d$ and two others which are symmetrically placed perpendicular to the triangle coming through its center with distance $2h$ between them.

The variational method is used to obtain all numerical results. Trial function is taken in a form of a symmetrized product of five 1s-Coulomb orbitals (Slater functions)

$$\psi_{g}^{(5Z,e)} = \tilde{S} e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3 - \alpha_4 r_4 - \alpha_5 r_5}, \quad (2)$$

where $\tilde{S}$ is symmetrizer with respect a permutation of charged centers. After doing permutations the trial function contains 120 terms. The function (2) depends on five $\alpha$’s variational parameters. It is expected that type of function gives results with an accuracy of $\sim 10^{-3}$ in total energy.

In order to find these critical charges, curves of the total energy as function of the charge can be obtained for the three different configurations, see Fig. 1. Calculations show that critical charges are $Z_{cr}^{\text{pentagon}} = 0.532$, $Z_{cr}^{\text{sqrtPyramid}} = 0.380$ and $Z_{cr}^{\text{Dipyramid}} = 0.350$ for pentagon, square pyramid and triangle dipyramid, respectively. Curves also show that the most stable geometrical configuration is given by the triangular dipyramid, see Fig. 2.

![Fig. 1: Total energy of systems $(5Z,e)$ as function of the charge $Z$ for three different configuration: Pentagon (solid line), square pyramid (long-dashed line) and triangular dipyramid (dashed line). Solid line ends at $Z_{cr}^{\text{pentagon}} = Z_{cr}^{(5Z,e)} = 0.532$. Long-dashed curve ends at $Z_{cr}^{\text{sqrtPyramid}} = Z_{cr}^{(5Z,e)} = 0.380$. Dashed curve ends at $Z_{cr}^{\text{Dipyramid}} = Z_{cr}^{(5Z,e)} = 0.350$](image)

![Fig. 2: System $(5Z,e)$. Charges are at vertices of geometric figure. The electron is at point $e$.](image)

For the optimal geometrical configuration, triangular dipyramid, it is possible to find the domains of metasta- bility; i.e. points where systems begin to have decay channels. These domains are given by crossing points between one-electron and $n Z$-charged systems, $(nZ,e)$. In Fig. 8 are shown curves of the total energy as function of the charge, $E(Z)$, for systems $(Z,e)$ (as reference curve), $(3Z,e)$, $(4Z,e)$ (see [2]), $(5Z,e)$ and $(6Z,e)$,
all taken in optimal configuration. Thus, for charges $Z \in (0.319, 0.350)$ the system is metastable with two decay channels

$$
(5Z, e) \rightarrow (3Z, e) + Z + Z
$$

(3)

For $Z \in (0.24, 0.319)$ system is metastable with one decay channel

$$
(5Z, e) \rightarrow (4Z, e) + Z
$$

(4)

And finally for $Z < 0.240$ the system is stable.

Beyond finding the critical charge, it is important to understand the behavior of the energy, as function of the charge, close to it. In this way it is found that this behavior is described by means of a Puiseux expansion

$$
E(Z) = \sum_{n=0}^{\infty} a_n(Z_{cr} - Z)^{b_n},
$$

(5)

with the condition that $b_n < b_{n+1}$. Where the goal is to find parameters $a_n$ and $b_n$ of this expansion. Restricting the expansion 5 to a finite number of terms a fit of the total energy calculated numerically. By making the fit, it is found that exponents $b_n$ are very close to $m/2$ ($m = 2, 3, 4, \ldots$); then, it is convenient to assume $b_n = m/2$ and only find the coefficients $a_n$. The fit is based on data from the domain $0 \leq Z \leq 0.345$ (10 points). This behavior indicates that critical point might be a square-root branch point.

$$
E(Z) = -0.3339 + 0.1636(Z_{cr} - Z)
$$

(6)

$$
- 2.1606(Z_{cr} - Z)^{3/2} + 15.1739(Z_{cr} - Z)^2
$$

$$
- 39.5356(Z_{cr} - Z)^{5/2} + \ldots,
$$

where the critical point is

$$
Z_{cr}(5Z, e) = 0.350.
$$

(7)

For the critical point $Z = 0$ (which is the singular point of the Schrödinger equation), and study the behavior of the energy as function of the charge. The behavior on the energy ($0 \leq Z \leq 0.15$ with 15 points) is given by Taylor expansion:

$$
E(Z) = -19.9541Z^2 + 109.699Z^3 - 207.039Z^4 + \ldots
$$

(8)

Such a behavior does not provide an indication to singular nature of the point $Z = 0$. However, the total energy can not be analytically continued to $\text{Re}Z < 0$.

Comparison between the results of fit of the energy 6 and fit 8 near critical charges $Z = Z_{cr}$, $Z = 0$, correspondingly, and data are shown in Table 1.

Finally, in Fig. 3 shows that the optimal geometrical configuration is a triangular dipyradim with equilateral triangular base, which height $h$ is always greater than the radius of maximal circular section of spheroid (circumscribed circle for the base) $R$. This tell us that the charges are situated on a prolate spheroid with semi-axis $R$, see Fig. 4. The form of spheroid changes with charge variation always remaining prolate.

**TABLE I:** Total energy of $(5Z, e)$, obtained with 6, compared with the result of the fit 8 (for $0.30 \leq Z \leq 0.345$) and 8 (for $0 \leq Z \leq 0.15$).

| $Z$ | $E_{cr}$ | Fit   |
|-----|---------|-------|
| 0.10 | -0.1113723 | -0.111545 |
| 0.11 | -0.1271357 | -0.127211 |
| 0.12 | -0.1428512 | -0.142783 |
| 0.13 | -0.1583834 | -0.158202 |
| 0.14 | -0.1736134 | -0.173462 |
| 0.15 | -0.1884371 | -0.188607 |
| 0.30 | -0.3265247 | -0.326525 |
| 0.31 | -0.3291843 | -0.329184 |
| 0.32 | -0.3311328 | -0.331133 |
| 0.33 | -0.3324624 | -0.332462 |
| 0.34 | -0.3332823 | -0.333282 |
| 0.35 | -0.3339403 | -0.333940 |

**FIG. 3:** Equilibrium geometrical configuration: Height of charges $h$ (solid line) and radius $R$ of circumscribed circle for charges fixed on vertices of equilateral triangle (dashed line), all as function of the charge $Z$.

**IV. SYSTEM $(6Z, e)$**

Now let us consider six fixed charges $Z$ and one electron. As in the five-center case, in this system there are infinite number of geometrical configurations among them there must exists one which is the optimal. It is possible to consider some of them, the most symmetric ones. Four configurations are considered: hexagon, the charges are placed on the vertices of the figure of side $L$ lying on the $x-y$ plane with the center in the origin of the plane and two charges on the $x$-axis; a pentagon pyramid, with five charges on the vertices of a pentagonal base of side $L$ and one charge at height $h$ on the perpendicular passing through the center; equilateral triangle dipyradim with three charges on the vertices of the triangle of side $L$, one charge in the center and other two on the perpendicular passing through the center of the triangle with distance...
2h between them; and finally a square dipyramid with four centers forming a square of side l, and two other lying on the perpendicular, passing through the center of the square, with distance 2h between them (octahedron).

The trial function for this case is taken in a form of a symmetrized product of six 1s-Coulomb orbitals (Slater functions)

$$\psi^{(6Z,e)}_g = \hat{S} e^{-\alpha_1 r_1 - \alpha_2 r_2 - \alpha_3 r_3 - \alpha_4 r_4 - \alpha_5 r_5 - \alpha_6 r_6},$$

where $\hat{S}$ is symmetrizer with respect a permutation of charged centers. After doing permutations the trial function (9) contains 720 terms, and depends on six $\alpha$’s variational parameters, given an accuracy of $\sim 10^{-3}$ in total energy.

Because of the complexity of the calculations and the loss of accuracy for small values of the charge, a energy curve is not possible to fully calculate, instead total energy is calculated for some given values of the charge. In Table II are shown total energy of the different configurations for some given values of the charge Z.

| Z     | Energy ($R_y$) |
|-------|----------------|
|       | SD  | TD  | PP  | Hexagon |
| 0.300 | -0.2855 | -0.2821 | -0.2539 | -0.2373 |
| 0.335 | -0.2749 | - | -0.2348 | -0.2125 |

TABLE II: Total energy as function of charge Z for various configurations of (6Z,e) system: square dipyramid (SD), triangular dipyramid (TD), pentagon pyramid (PP) and hexagon. For Z = 0.335 the triangular dipyramid does not exist.

From Table II it is seen that among configurations studied the square dipyramid presents the lowest total energy, and it is possible to say that this configuration is the optimal one for the (6Z,e) system.

For the optimal configuration, see Fig. 5 it is found that the critical charges which separate the domain of existence from non-existence of the bound state are at $Z = 0$ and $Z_{cr} = 0.335$. Thus, the system $(6Z,e)$ can exist for charges $0 < Z < Z_{cr}$. In Fig. 8 is shown the total energy as function of the charge at equilibrium distances $l_{eq}$ and $h_{eq}$. From Fig. 8 we can see the crossing points with other curves, that give us the domains of metastability of the system.

The domains of metastability are given in the following way: for charges $Z \in (0.2879, 0.3350)$ the system is metastable with three decay channels

$$\begin{align*}
(6Z,e) &\rightarrow (3Z,e) + Z + Z + Z \\
(6Z,e) &\rightarrow (4Z,e) + Z + Z \\
(6Z,e) &\rightarrow (5Z,e) + Z
\end{align*}$$

(10)

For $Z \in (0.2358, 0.2879)$ system is metastable with two decay channel

$$\begin{align*}
(6Z,e) &\rightarrow (4Z,e) + Z + Z \\
(6Z,e) &\rightarrow (5Z,e) + Z
\end{align*}$$

(11)

For $Z \in (0.2318, 0.2358)$ system is metastable with the single decay channel

$$(6Z,e) \rightarrow (5Z,e) + Z,$$ \hspace{1cm} (12)

and, finally, for $Z < 0.2318$ the system is stable.

Behavior of the energy as function of the charge close to critical charge $Z_{cr}$ is given by the following Puiseux expansion

$$E(Z) = -0.2749 - 0.0763(Z_{cr} - Z) - 3.7767(Z_{cr} - Z)^{3/2} + 22.813(Z_{cr} - Z)^2 - 54.9039(Z_{cr} - Z)^{5/2}$$

(13)

where the critical point is

$$Z_{cr}^{(6Z,e)} = 0.335.$$ \hspace{1cm} (14)

The result of fit is based on data from the domain $0.32 \leq Z \leq 0.33$ (20 points). This behavior indicates that critical point might be a square-root branch point with exponent 3/2.
For the critical point \( Z = 0 \) the behavior on the energy \((0 \leq Z \leq 0.15 \) with 15 points\) is given by Taylor expansion:

\[
E(Z) = -28.1767Z^2 + 184.321Z^3 - 405.044Z^4 + \ldots (15)
\]

Such a behavior does not provide an indication to singular nature of the point \( Z = 0 \). However, the total energy cannot be analytically continued to \( \text{Re} Z < 0 \).

Comparison between the fits of the energy (13) and (15) near critical charges \( Z = Z_{cr}, Z = 0 \) and data are shown in Table III.

| \( Z \)   | \( E_T \)    | Fit          |
|----------|--------------|--------------|
| 0.1000   | -0.1376189   | -0.13795     |
| 0.1100   | -0.1549053   | -0.15491     |
| 0.1200   | -0.1715792   | -0.17123     |
| 0.1300   | -0.1874736   | -0.18692     |
| 0.1400   | -0.2024490   | -0.20209     |
| 0.1500   | -0.2163915   | -0.21639     |
| 0.320    | -0.2793243   | -0.279328    |
| 0.322    | -0.2786595   | -0.278657    |
| 0.324    | -0.2779993   | -0.277997    |
| 0.326    | -0.2773488   | -0.277350    |
| 0.328    | -0.2767147   | -0.276718    |
| 0.330    | -0.2761066   | -0.276108    |

TABLE III: Total energy of \((6Z, e)\), obtained with (9), compared with the result of the fit (13) (for \(0.320 \leq Z \leq 0.330\)) and (15) (for \(0 \leq Z \leq 0.15\)).

Finally, it is presented in Fig. 6 curves of the distances (height \( h \), and radius of circumscribed circle \( R \)) as functions of the charge \( Z \) for the geometrical configuration of the system (octahedron).

From Fig. 6 we see that the optimal geometrical configuration is an octahedron, which height \( h \) is always smaller than the radius of circumscribed circle \( R \). This tell us that the charged are placed on a oblate spheroid with semi-axes \( R \), see Fig. 7.

**V. CONCLUSIONS**

In this paper it is calculated for the first time the critical charges for two molecular systems: \((5Z, e)\) and \((6Z, e)\). It is found that for all those systems the total energy and equilibrium distances vs \( Z \) are smooth curves without any indication to charge quantization. It is also found that the optimal geometric configuration seems always to be the maximally symmetric: Being a triangular dipyramid for \((5Z, e)\) and octahedron for \((6Z, e)\).

It is important to mention that the behavior near critical charge of total energy as function of the charge, \( E(Z) \), indicates a square-root branch point with exponent 3/2.
This agrees with what was previously found for various atomic and molecular systems \[2\].

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[1] A. V. Turbiner and J. C. Lopez Vieyra, *Phys. Rep.* **424**, 309-396 (2006)
[2] A. V. Turbiner and H. Medel Cobaxin, *Int. J. Quantum Chem.* **112**, 2411 (2012)
[3] J. Schwinger, *Phys. Rev.* **D12**, 10 (1975)
[4] A. Herdegen, *Act. Phys. Pol.* **B14**, 12 885-892 (1983)
[5] B. Simon, *J. Funct. Anal.* **25**, 338 (1977).
[6] T. K. Rebane, *Sov. Phys. JEPT* **71**, 1055 (1995)
[7] Q. Shi and S. Kais, *Mol. Phys.* **98**, 1485 (2000)
[8] A.V. Turbiner, *Usp. Fiz. Nauk.* **144**, 35 (1984)

*Sov. Phys. – Usppekhi** **27**, 668 (1984) (English Translation)
[9] A.V. Turbiner, *Yad. Fiz.* **46**, 204 (1987)

*Sov. Journ. of Nucl. Phys.* **46**, 125 (1987) (English Translation)
[10] A.V. Turbiner and J.C. Lopez Vieyra, *Phys. Rev.* **A66**, 023409 (2002)
[11] L. Pauling, *J. Chem. Phys.* **56**, 1 (1933)

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