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# INVESTIGATION OF THE BOUNDARY CONDITIONS INFLUENCE ON THE GROUND STATE PROPERTIES OF A TWO-ELECTRON ATOM IN A CAVITY

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**Summary.** The conditions under which the two-electron atom with atomic number $Z \geq 2$ placed in the spherical cavity could either be in stable state or decay into the one-electron atom with same atomic number and an electron are studied. It is shown that the binding and ionization energies of the two-electron atom in a cavity with certain parameters of its boundary could be substantially bigger than the corresponding energies of the free one, which means that effective containers for such atoms can exist. By analogy with the Wigner-Seitz model the possibility of interpreting of such cavities as a kind of the Wigner-Seitz cells and forming a spatial lattice of such cavities filled by the two-electron atoms is discussed.

## 1 INTRODUCTION

Since the early days of quantum mechanics the study of two-electron atom is of particular interest because it is the simplest example of the quantum system with the Coulomb repulsion between electrons. For atomic number $Z \geq 2$ the ground state energy of the free two-electron atom was already obtained with good accuracy in 1928 by Hartree[1] and over the next few years the further researches by Bethe[2] and Hylleraas[3] allowed to obtain the ground state energy for $Z = 1$. The development of new technologies and experimental techniques has triggered intensive theoretical studies of the confined two-electron atom, which provide a lucid way to study the effect of confinement on the electron correlation which arises due to the Coulomb interaction between electrons and the Pauli exclusion principle[4-14].

In this work the ground state properties of the two-electron atom with $Z \geq 2$ in a vacuum microcavity with the most general conditions which provide confinement of electrons inside the cavity are considered. More specific, the influence of such conditions on the behavior of the ground state energy for $Z = 2$ (helium atom $He$) and $Z = 3$ (positive lithium ion $Li^+$) as a function of cavity spatial parameters is studied. In many tasks of quantum chemistry and condensed matter physics[4, 15-24] the general conditions do not require the obligatory vanishing of a wave function at the cavity boundary as in the case of atoms trapped in the cavity by an impermeable or partially permeable potential barrier imitating the compression mode by the external pressure (see Refs. [4]-[5], [7]-[13], [14] and references therein). In particular, in some cases the Neumann conditions imposed on the wave function on the cavity boundary could provide not only the confinement of electrons inside the cavity but also the periodic continuation of the wave function as in the Wigner-Seitz model of alcaline metal[21]. Thus, similar to interstitial sites in the crystal matrix[25] the empty cavities could form a spatial lattice, where each cavity will correspond to the Wigner-Seitz cell. When the whole lattice of cells is occupied by atoms of the same type, atomic electrons find themselves in a periodic potential

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and so the description of their ground state could be based on the principles of the Wigner-Seitz model. The influence of such boundary conditions on the ground state of the confined one-electron atoms was studied in [22] - [24]. The rest of this work is organized as follows: in Section 3 the two-electron atom is considered in the spherical cavity with $\delta$-like potential at the boundary which corresponds to the third type boundary conditions imposed on the wave function on the cavity boundary and in Section 4 more realistic case, where atomic electrons are trapped in the cavity by means of an outer potential shell of non vanishing width with the Neumann conditions imposed on the wave function on its outer boundary, is described. For both cases it is shown that under certain conditions the two-electron atom in the cavity could be in the ground state with binding and ionization energies, which are substantially bigger than the corresponding energies of the free atom or decay into the one-electron atom with the same atomic number and an electron.

## 2 CONFINEMENT OF THE TWO-PARTICLE QUANTUM SYSTEM IN A CAVITY

The non relativistic energy functional of two quantum particles with mass *m*, which are confined in a cavity Ω with boundary Σ by means of $\delta$-like potential, could be written as follows

$$E[\Psi] = \int\limits_{\Omega} dV_1 dV_2 \left[\frac{\hbar^2}{2m}\left|\vec{\nabla}_1\Psi\right|^2 + \frac{\hbar^2}{2m}\left|\vec{\nabla}_2\Psi\right|^2 + \left\{\widetilde{U}(\vec{r}_1) + \widetilde{U}(\vec{r}_2) + W(\vec{r}_1,\vec{r}_2)\right\}|\Psi|^2\right] \tag{1}$$

where

$$\widetilde{U}(\vec{r}) = U(\vec{r}) + \frac{\hbar^2}{2m}\lambda(\vec{r})\delta_{\Sigma}(\vec{r}) \tag{2}$$

Here $U(\vec{r})$ is the potential field inside Ω and the surface $\delta$-function $\delta_{\Sigma}(\vec{r})$ together with a real function $\lambda(\vec{r})$ defines a contact interaction of the particles with medium, in which the cavityhas been formed, at the boundary Σ. Potential $W(\vec{r}_1,\vec{r}_2)$ describes the interaction between the particles.

From the variational principle with the normalization condition

$$\langle\Psi|\Psi\rangle = \int_{\Omega} dV_1 dV_2 |\Psi|^2 \tag{3}$$

follows the equation inside the cavity Ω

$$\left[-\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 + U(\vec{r}_1) + U(\vec{r}_2) + W(\vec{r}_1,\vec{r}_2)\right]\Psi = E\Psi \tag{4}$$

together with third type boundary conditions on the cavity surface Σ

$$\begin{aligned}\left[\left(\vec{n}_1\vec{\nabla}_1\right) + \lambda(\vec{r}_1)\right]\Psi(\vec{r}_1,\vec{r}_2)\big|_{\vec{r}_1\in\Sigma} = 0\\ \left[\left(\vec{n}_2\vec{\nabla}_2\right) + \lambda(\vec{r}_2)\right]\Psi(\vec{r}_1,\vec{r}_2)\big|_{\vec{r}_2\in\Sigma} = 0\end{aligned} \tag{5}$$

where the outward normal to the surface Σ is denoted by $\vec{n}$.

If the contact interaction of the particles with cavity environment at Σ is absent, $\lambda = 0$ and the conditions (5) transform into Neumann boundary conditions

$$\left(\vec{n}_1\vec{\nabla}_1\right)\Psi(\vec{r}_1,\vec{r}_2)\big|_{\vec{r}_1\in\Sigma} = 0\,,\left(\vec{n}_2\vec{\nabla}_2\right)\Psi(\vec{r}_1,\vec{r}_2)\big|_{\vec{r}_2\in\Sigma} = 0 \tag{6}$$

The boundary conditions (6) could describe not only the confinement of the quantum particles in the cavity Ω, but also the periodic continuation of the wavefunction whichprovides the opposite situation - delocalization of the particles. For example, in the Wigner-Seitz model of an alkaline metal such delocalization of the particles gives rise to metallic bonding[20]. Therefore, such a "confinement" state is of special interest because in ordered structures vacuum cavities of the same type could form a spatial lattice. However, in this case the presence of the contact interaction is required because the particles are placed in the cavity formed in a medium and the contact interaction of the particles with environment exist. And if $\lambda \to \infty$, then (5) turn into the Dirichlet boundary conditions

$$\Psi(\vec{r}_1,\vec{r}_2)|_{\vec{r}_1\in\Sigma} = 0\,,\Psi(\vec{r}_1,\vec{r}_2)|_{\vec{r}_2\in\Sigma} = 0 \tag{7}$$

and so describe confinement by impenetrable barrier.

## 3 STABILITY CONDITIONS OF THE TWO-ELECTRON ATOMS WITH $Z \geq 2$ IN THE SPHERICALLY SYMMETRIC CAVITY

As an example of a two-particle system one can consider a two-electron atom with atomic number $Z$. One can assume that the point nucleus is arranged in the center of asphericaly symmetric cavity of radius $R$ and the contact interaction of the electrons with cavity environment is defined by a constant $\lambda = const$. In the Hartree-Fock approximation the form of ansatz for the ground state of the two-electron atom could be written as follows

$$\Psi(\vec{r}_1,\vec{r}_2) = \phi(r_1)\phi(r_2) = \frac{u(r_1)u(r_2)}{r_1 r_2} \tag{8}$$

Where $\phi(r)$ corresponds to one-electron wavefunction. It should be noted that this ansatz does not allow obtaining accurate values of the ground state energy, but it is adequate for the qualitative study of the lowest energy level of the two-electron atom with $Z \geq 2$ in a confinement state as a function of cavity spatial parameters.

In what follows, in order to simplify the notation, the relativistic units will be used: $\hbar = c = 1$, wave number and energy will be expressed in units of the particle mass $m$, while distances in units of the particle Compton length $1/m$. In these units the energy functional (1) is given by

$$E[u] = \int_0^R dr\left\{[u'(r)]^2 - \frac{2Z\alpha}{r}u^2(r)\right\} + \tag{9}$$
$$2\alpha\int_0^R dr_2\frac{u^2(r_2)}{r_2}\int_0^{r_2} dr_1 u^2(r_1) + \left(\lambda - \frac{1}{R}\right)u^2(R)$$

with the normalization condition

$$\int_0^R dr\, u^2(r) = 1 \tag{10}$$

The boundary conditions (5) on the cavity surface Σ transform into

$$R\,u'(R) + (\lambda R - 1)u(R) = 0 \tag{11}$$

Now the direct variational method can be applied. For this purpose, the interval $[0, R]$ is divided into $N$ equal parts of length $h_R$, and the energy functional (9) turns into a discrete one. With the boundary condition (11) one obtains instead of the energy functional (9) an algebraic function of the variables $u_i = u(h_R \cdot i)$ where $i = 1, .., N-1$, which is restored back into the functional (9) at $N \to \infty$. Using the conjugate gradient method under the condition (10) one can minimize the algebraic function to determine the ground state energy of the two-electron atom with sufficient accuracy for a qualitative description of its behavior depending on the parameters $R$ and $\lambda$ at $Z \geq 2$. For example, for the atom with $Z = 2$ in the cavity with the Dirichlet boundary conditions (7) the difference between the ground state energy obtained by using the method described above, and the energy obtained by amore precise calculation in [9], is less than $2\ eV$.

Now let's investigate the asymptotic behavior of the lowest energy level as a function of the cavity spatial parameter $R$ for fixed $\lambda$ at $R \to 0$. It should be noted that in order toremain within the framework of a purely Schroedinger approximation it is necessary to limit the minimal cavity size by $R{\sim}10$ (see Ref. [24]). Therefore, the limit of $R \to 0$ is to be understood either as a purely mathematical operation, or as the substitution of $R{\sim}10$. According to [22] - [24] a wavefunction of the one-electron atom in the cavity with the contact potential at the boundary inside the cavity corresponds to the solution of the Schroedinger equation for bound states of an electron in the potential field of a fixed point nucleus. Therefore, at $R \to 0$ the function in the ansatz (5) could be considered as a constant. In this case, with the normalization condition (10) the lowest energy level behaves asymptotically at $R \to 0$ as follows

$$\hat{E}_{2el}(Z, R) = \frac{3(\lambda - Z\alpha)}{R} + \frac{6}{5}\frac{\alpha}{R} \tag{12}$$

It is easily seen from (12) that the lowest energy level behaves substantially different depending on the value of $\lambda$ at $R \to 0$. Most specific behavior of the lowest energy level at $R \to 0$ will be in case $\lambda = \lambda^s_{2el}(Z)$, where $\lambda^s_{2el}(Z) = (Z - 2/5)\alpha$ – in this case the ground state energy converges to a finite value. At $\lambda > \lambda^s_{2el}(Z)$, the ground state energy increases when decreases $R$, and vice versa at $\lambda < \lambda^s_{2el}(Z)$.

It could be assumed that the asymptotic behavior of the lowest energy level at $R \to \infty$ might meet the results obtained in [22]-[24]. Therefore, there are two types of asymptotic behavior of the lowest level in dependence on $\lambda$. The first type takes place when the lowest level exponentially fast approaches the ground state energy of the two-electron atom $E_{2el}(Z)$ (such levels will be denoted as $E_{2el}(Z, R)$). And the second type takes place when the lowest level approaches $\tilde{E}_{2el}(Z) \leq E_{2el}(Z)$ (from this point such levels will be denoted as $\tilde{E}_{2el}(Z, R)$). The last type is possible only when the contact potential attracts electrons. In this case, at $R \to \infty$ electrons are localized near the cavity boundary, and the Coulomb electron-electron and electron-nucleus interactions become negligible in comparison with the boundary attraction. Therefore, for $\lambda = const$ the asymptotic value $\tilde{E}_{2el}(Z)$ corresponds to the doubled ground state energy of an electron in the spherical cavity at $R \to \infty$

$$\tilde{E}_{2el}(Z) = -\lambda^2 \tag{13}$$

Where $\lambda \leq \lambda_{2el}^{crit}(Z) < 0$ and $\lambda_{2el}^{crit}(Z) = -\sqrt{|E_{2el}(Z)|}$. The asymptotic behavior of those levels should be power.

Indeed, as shown in Fig. 1 for $Z = 2; 3$ and positive $\lambda = x\lambda_{2el}^{s}(Z)$ with $x = 1/2; 1; 3/2$ exponential levels $E_{2el}(Z, R)$ closely approach $E_{2el}(Z)$ for $R$ of order of several Bohr radii $a_B \simeq 1/137$, where $E_{2el}(Z) = -(Z - 5/16)^2\alpha^2$ in the approximation (8). The lowest power levels $\tilde{E}_{2el}(Z, R)$ correspond to $\lambda = \lambda_{2el}^{crit}(Z)$ and sufficiently slower than that of the exponential ones converge to $\tilde{E}_{2el}(Z) = E_{2el}(Z)$ with increasing $R$. Also for $\lambda = \lambda_{2el}^{s}(Z)$ it is shown that in most specific case the lowest level $E_{2el}(Z, R)$ converges to $E_{2el}(Z)$ at $R \to 0$. It should be noted that in Fig. 1 the minimum size of the cavity is limited from bellow $R \geq 10$ to remain within the framework of the purely Schroedinger approximation. The same limitation is presented in all subsequent figures.

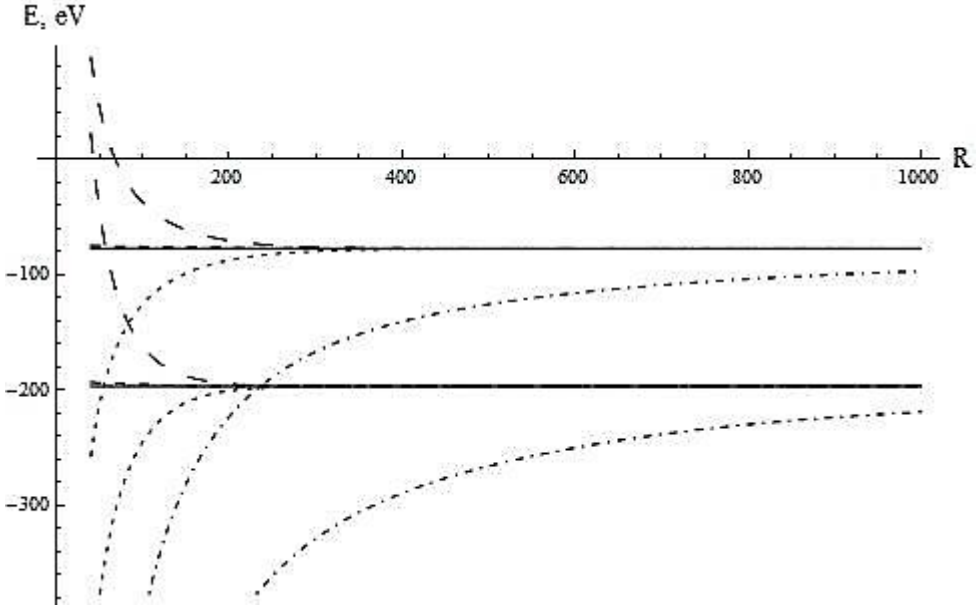


Fig. 1: The lowest level of the two-electron atom with $Z = 2; 3$ as a function of cavity radius $R$ for $\lambda = x\lambda_{2el}^{s}$with $x = 1/2$ (dotted line), 1(short-dashed line), 3/2 (long-dashed line), $\lambda = x\lambda_{2el}^{crit}$ (dot-dashed line); $E_{2el}(Z)$ (solid line)

Next, one can explore the stability of the two-electron atom with atomic number $Z \geq 2$ in the cavity. For further discussion some information about the asymptotic behavior of the one-electron atom lowest level is required. From [23], for example, it is known that at $R \to 0$ the one-electron atom lowest level behaves as

$$\hat{E}_{1el}(Z, R) = \frac{3}{2}\frac{(\lambda - Z\alpha)}{R} \tag{14}$$

It is easily seen from (14) that the most specific behavior of the one-electron atom lowest level, when it converges at $R \to 0$ to a finite value, will be in case $\lambda = \lambda_{1el}^{s}(Z)$, where $\lambda_{1el}^{s}(Z) = Z\alpha$. In fact, $E_{1el}(Z, R) = E_{1el}(Z)$ for such value of $\lambda$ and any $R$, where $E_{1el}(Z) = -(Z\alpha)^2/2$ is the ground state energy of the free one-electron atom with atomic number $Z$. At

$\lambda > \lambda_{1el}^{s}(Z)$ the ground state energy increases when decreases $R$, and vice versa at $\lambda < \lambda_{1el}^{s}(Z)$. At $R \to \infty$ the exponential levels $E_{1el}(Z,R)$ approach $E_{1el}(Z)$, and the power levels $\tilde{E}_{1el}(Z,R)$ approach

$$\tilde{E}_{1el}(Z) = -\lambda^2/2 \tag{15}$$

Where $\lambda \le \lambda_{1el}^{crit}(Z) < 0$ and $\lambda_{1el}^{crit}(Z) = -\sqrt{2|E_{1el}(Z)|}$.

It follows from (12) and (14) that for $\lambda = (Z - 4/5)\alpha$ the asymptotes $\hat{E}_{1el}(Z,R)$ and $\hat{E}_{2el}(Z,R)$ coincide, i.e. when $\lambda < (Z - 4/5)\alpha$ the binding energy of the one-electron atom should be smaller than the binding energy of two-electron atom with the same $Z$ at $R \to 0$, and vice versa when $\lambda > (Z - 4/5)\alpha$. Thus, for $\lambda > (Z - 4/5)\alpha$ always exists such a cavity, although small in size, in which the two-electron atom decays into the one-electron atom and an electron. This fact is explicitly shown in Fig. 2a, where the behavior of the one- and two-electron atoms for $\lambda = (3/2)\lambda_{2el}^{s}(Z)$ is displayed.

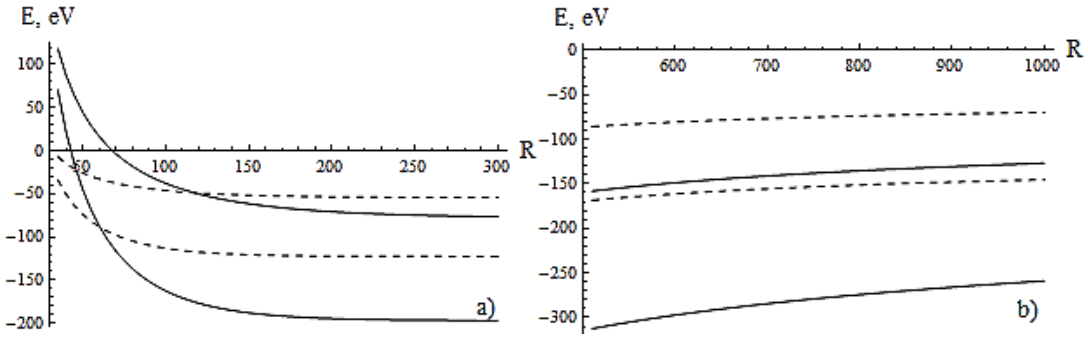


Fig. 2: The lowest levels of the two-electron atom (solid line) and of the one-electron atom (dotted line) with $Z = 2; 3$ as a function of cavity radius $R$ for $\lambda = (3/2)\lambda_{2el}^{s}(Z)$ (a) and $\lambda = \lambda_{1el}^{crit}(Z)$ (b)

On the other hand, the exponential level $E_{2el}(Z,R)$ converges to $E_{2el}(Z)$, and the power level $\tilde{E}_{2el}(Z,R)$ converges to $\tilde{E}_{2el}(Z) \le E_{2el}(Z)$ at $R \to \infty$. In particular, for $\lambda > (Z - 4/5)\alpha$ with increasing $R$ the curves $E_{2el}(Z,R)$ and $E_{1el}(Z,R)$ intersect, and the ionization energy of the two-electron atom converges to the value $E_{1el}(Z,R) - E_{2el}(Z,R)$ at $R \to \infty$. For $\lambda < (Z - 4/5)\alpha$ the two-electron atom remains stable for any$R$. And for $\lambda_{2el}^{crit} < \lambda < (Z - 4/5)\alpha$ the lowest levels of the one- and two-electron atoms are exponential, and the ionization energy of the two-electron atom with increasing $R$ converges to $E_{1el}(Z) - E_{2el}(Z)$. For $\lambda_{1el}^{crit} < \lambda \le \lambda_{2el}^{crit}$ only the lowest level of the two-electron atom is already power, and for $\lambda \le \lambda_{1el}^{crit}$ not only the level of the two-electron atom is already power but also the level of the one-electron one. In this case the ionization energy of the two-electron atom with increasing $R$ slowly approaches the values $E_{1el}(Z) - \lambda^2$ and $\lambda^2/2$, respectively, as shown in Fig. 2b for $\lambda = -Z\alpha$ at $Z = 2; 3$.

Thus, for $\lambda > (Z - 4/5)\alpha$ it is possible that the two-electron atom in the cavity decays into the one-electron atom and an electron. At the same time, for $\lambda < (Z - 4/5)\alpha$ the ionization and binding energies of the atoms in the cavity can be substantially bigger than the corresponding energies of the free ones, and hence such the cavities are effective containers for the two-electron atoms.

## 4 STABILITY CONDITIONS OF THE TWO-ELECTRON ATOMS WITH $Z \geq 2$ IN THE CAVITY WITH AN OUTER SHELL OF NONVANISHING WIDTH

Up to this point it was assumed that atomic electrons interact with cavity environment only at its boundary Σ by means of $\delta$-like potential. In a more realistic approach one should consider instead of a $\delta$-like interaction an outer potential shell of non vanishing width $d$, into which the electrons penetrate and interact there with cavity environment. In the simplest case, the outer shell potential could be approximated by a constant $V_0$, i.e. one should assume that the interaction between electrons and nucleus and the Coulomb repulsion between electrons are completely screened in the shell. Such a potential is related to atomic physics and is used, for example, for simulating the $C_n$ cage in the electronic structure studies of endohedral fullerenes[15,26]. The constant $V_0$ should depend on the shell width $d$ so that in the limit $d \to 0$ such a potential shell should transform into contact interaction at the boundary Σ

$$V_0 d \to \frac{\hbar^2}{2m}\lambda\,, \qquad d \to 0 \tag{16}$$

Notice that the limits $d \to 0$ and $V_0 \to \infty$ don't commute, because when$d$ is finite and $V_0 \to \infty$ one obtains the confinement of the atom by an impermeable barrier instead of the contact interaction at the boundary Σ.

In the spherically symmetric case with a constant potential in the shell instead of boundary conditions (5) one obtains an equation of Schroedinger type

$$\left[-\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 + 2V_0\right]\Psi = E\Psi\,, \qquad R \leq r \leq X = R + d \tag{17}$$

with Neumann conditions on the outward shell boundary

$$\frac{\partial}{\partial r_1}\Psi(\vec{r}_1,\vec{r}_2)\Big|_{r_{1=X}} = 0\,, \qquad \frac{\partial}{\partial r_2}\Psi(\vec{r}_1,\vec{r}_2)\Big|_{r_{2=X}} = 0 \tag{18}$$

In such a model, the interaction of electrons with cavity environment is defined by the equation (17), so $\lambda$ is absent in (18). Boundary conditions (18) could provide not only the confinement of the electrons in the cavity Ω, but also the periodic continuation of the wave function. Therefore, if real microcavitymight be approximated by a spherically symmetric cavity with an outer shell, the ground state of charged particles in a cubic lattice, formed by cavities of the same type, could be described as in the Wigner-Seitz model[21]. The well-known example of such lattices is given by octahedral and tetrahedral interstitial sites in certain metals and alloys[25,27,28]. The cavity together with the outer shell forms a kind of the Wigner-Seitz cell, while the boundary conditions (18) provide a periodic extension of the wave functions between neighboring cells.

In view of the above the energy functional (9) transforms into the form

$$E[u] = \int_0^X dr[u'(r)]^2 - 2Z\alpha\int_0^R dr\frac{u^2(r)}{r} + \tag{19}$$
$$2\alpha\int_0^R dr_2\frac{u^2(r_2)}{r_2}\int_0^{r_2} dr_1 u^2(r_1) + 2V_0\int_R^X dr\, u^2(r) - \frac{u^2(X)}{X}$$

and the normalization condition (10) takes the form

$$\int_0^X dr\, u^2(r) = 1 \tag{20}$$

The Neumann boundary conditions (18) turn into

$$X\, u'(X) = u(X) \tag{21}$$

Now let's investigate the asymptotic behavior of the lowest energy level as a function of the cavity and shell spatial parameters$R$ and $d$ at $R \to 0$ and $d \to 0$. In this case, thelimits $R \to 0$ and $d \to 0$ are also to be understood as either purely mathematical operation, or as the substitution of $R{\sim}10$ and $d{\sim}10$. As in the previous section, at $R \to 0$ the function $\phi(r)$ in the ansatz (5) inside the cavity could be considered as a constant. The function $\phi(r)$ in the outer shell at $R \to 0$corresponds to the problem of an electron inside the potential barrier of finite height $V_0$ and width$d$ with Neumann condition on the outer shell boundary.Therefore, in the shell $\phi(r)$ at $R \to 0$ and $d \to 0$ could also be considered as a constant. This means that the lowest energy level behaves asymptotically with the normalization condition (20) at $R \to 0$ as follows

$$\hat{E}_{2el}(Z,R) = -3Z\alpha\frac{R^2}{X^3} + 2V_0\left(1 - \frac{R^3}{X^3}\right) + \frac{6}{5}\alpha\frac{R^5}{X^6} \tag{22}$$

and the limit of (22) at $R \to 0$ is the value $2V_0$.

There are two types of asymptotic behavior of the lowest level at $R \to \infty$ in dependence on outer shell parameters in analogy with the previous section. The limit of the exponential lowest levels $E_{2el}(Z,R)$ is $E_{2el}(Z)$ and the limit of the power lowest levels $\tilde{E}_{2el}(Z,R)$ is $\tilde{E}_{2el}(Z) \le E_{2el}(Z)$, which corresponds to the doubled ground state energy of an electron in the attractive potential $V_0 < 0$

$$\tilde{V}(r) = \begin{cases} 0\ , 0 < r < R \\ V_0\ , R \le r < X \end{cases} \tag{23}$$

at $R \to \infty$. Thus, according to [23] one can obtain the limit $\tilde{E}_{2el}(Z)$ by solving the equation

$$\sqrt{2|V_0| + \tilde{E}_{2el}(Z)}\,\tan\left(\sqrt{2|V_0| + \tilde{E}_{2el}(Z)}\cdot d\right) = \sqrt{-\tilde{E}_{2el}(Z)} \tag{24}$$

Now one can investigate the asymptotic behavior of the lowest energy level as a function of the cavity spatial parameter$R$ using the numerical minimization results of the energy functional (19) under the conditions (20) and (21) for fixed $V_0$and$d$. Parameters of the outer shell are selected to correspond to the scales of the actual conditions of microcavities, in which such a confinement state is possible (from this point the energy potentials are expressed in$eV$). The values of $|V_0|$ could vary from $\sim 1\ eV$ in superfluid helium[29] and $\sim 5 - 10\ eV$ for interstices in metal lattices[27, 28] up to dozens $eV$ in quantum chemistry[4, 14-18]. For example, as one of the characteristic values of $V_0$can be chosen the positive average value $V_0 = 10\ eV$. In this case the ground state energy coincides with the exponential lowest level. Also another case of interest arises when in the outer shell acts the "critical" potential $V_0 = V_{2el}^{crit}(Z)$ and the lowest level turns out to be the power one $\tilde{E}_{2el}(Z,R)$. The values of such a potential can

be determined by solving (24) with the substitution $\tilde{E}_{2el}(Z) = E_{2el}(Z)$. Since the calculations are performed within the approximation (8) then $E_{2el}(Z) = -(Z - 5/16)^2\alpha^2$. The numerical values of $V_{2el}^{crit}(Z)$ for $d = x\ a_B$with $x = 1/4\,, 1/2, 1$ and $Z = 2; 3$ are presented in Tab. 1.

| | $Z=2$ | | | $Z=3$ | | |
|---|---|---|---|---|---|---|
| $x = d/a_B$ | $1/4$ | $1/2$ | $1$ | $1/4$ | $1/2$ | $1$ |
| $V_{crit}\,, eV$ | $-119.74$ | $-74.59$ | $-53.07$ | $-218.1$ | $-148.33$ | $-116.72$ |

Tab. 1:The values of $V_{2el}^{crit}(Z)$ for $d = x\ a_B$

For $Z = 2; 3$ and the outer shell width $d = x\ a_B$ with $x = 1/4\,, 1/2, 1$ for $V_0 = 10\ eV$ there are minima in curves $E_{2el}(Z, R)$ and the minimum depth increases while$d$ decreases as shown in Fig. 3a. For example, for $Z = 2$ and $d = a_B/4$ the minimum is clearly pronounced, but it is already pronounced rather weakly at $d = a_B/2$. And for $d = a_B$ the maximal binding energy of the two-electron atom will be attained at large cavity radii $R \gg a_B$. As a consequence while filling a spatial lattice, formed by such a microcavities, with two-electron atoms, the bulk compression or extension is possible as it occurs upon hydrogenation of some metals[25, 27, 28]. Furthermore, as it is shown in Fig. 3a the limits of the curves $E_{2el}(Z, R)$ and of the asymptotes (22) coincide and are equal to $2V_0 = 20\ eV$ at $R \to 0$. Fig. 3b shows that for $V_0 = V_{2el}^{crit}(Z)$ the difference between $\tilde{E}_{2el}(Z) = E_{2el}(Z)$ and the power lowest levels decrease sufficiently slower than that of the exponential ones, which already arrive at $E_{2el}(Z)$ for $R$ of order of several $a_B$ as shown in figure 3a.

Next, one can explore the stability of the two-electron atom with atomic number $Z \geq 2$ in the cavity with the spherical outer shell of non vanishing width. For further discussion some information about the asymptotic behavior of the one-electron atom lowest level is required. From [23], for example, it is known that at $R \to 0$ the limit of the one-electron atom lowest level is $V_0$ for any$d$. At $R \to \infty$ the exponential lowest levels $E_{1el}(Z, R)$ converge to $E_{1el}(Z)$ and the power ones $\tilde{E}_{1el}(Z, R)$ arrive to $\tilde{E}_{1el}(Z) \leq E_{1el}(Z)$, which for attractive potential $V_0 < 0$ can be defined from the equation

$$\sqrt{2|V_0| + 2\tilde{E}_{1el}(Z)}\,\tan\left(\sqrt{2|V_0| + 2\tilde{E}_{1el}(Z)}\cdot d\right) = \sqrt{-2\tilde{E}_{1el}(Z)} \tag{25}$$

The corresponding values of the "critical" potential for the one-electron atoms, while the lowest level turns out to be the power one, and for $d = x\ a_B$with $x = 1/4\,, 1/2, 1$ are presented in Table 2.

| | $Z=2$ | | | $Z=3$ | | |
|---|---|---|---|---|---|---|
| $x = d/a_B$ | $1/4$ | $1/2$ | $1$ | $1/4$ | $1/2$ | $1$ |
| $V_{crit}\,, eV$ | $-148.19$ | $-95.13$ | $-70.24$ | $-253.27$ | $-176.23$ | $-141.87$ |

Tab. 2:The values of $V_{1el}^{crit}(Z)$ for $d = x\ a_B$

Considering the above, when $V_0 > 0$ for any$d$ at $R \to 0$ the lowest energy level of the two-electron atom will lie above the lowest level of the one-electron atom and vice versa for $V_0 < 0$.

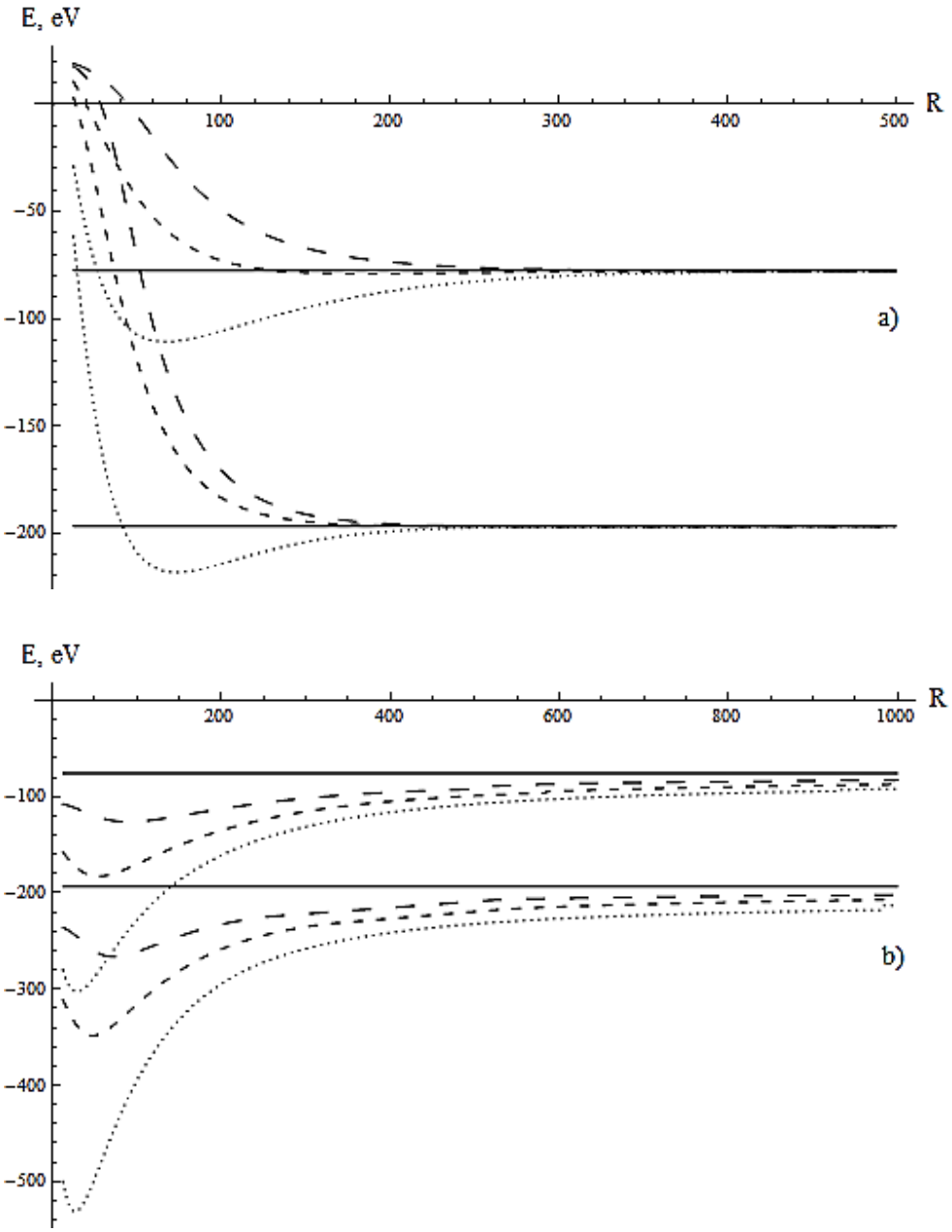


Fig. 3: The lowest level of the two-electron atom with $Z = 2; 3$ as a function of cavity radius $R$ at $V_0 = 10\ eV$ (a) and $V_0 = V_{2el}^{crit}(Z)$ (b) for $d = xa_D$ with $x = 1/4$ (dotted line),$1/2$ (short-dashed line),1 (long-dashed line);$E_{2el}(Z)$ (solid line)

On the other hand, taking into account (24), (25), at $R \to \infty$ for any $V_0$ and $d$ the lowest energy level of the two-electron atom will lie below the lowest level of the one-electron atom. Numerical calculations show that for any fixed $V_0 > 0$ curves $E_{2el}(Z, R)$ and $E_{1el}(Z, R)$ intersect and this intersection point moves toward the large values of $R$, while$d$ increases, as shown in Fig. 4. Furthermore, in dependence on the outer shell parameters $V_0 > 0$ and $d$ it is possible that the two-electron atom in the cavity decays into the one-electron atom and an electron (see Fig. 4b) or vice versa the ionization and binding energies of such an two-

electron atom can be substantially bigger than the corresponding energies of the free one (see Fig. 4a).

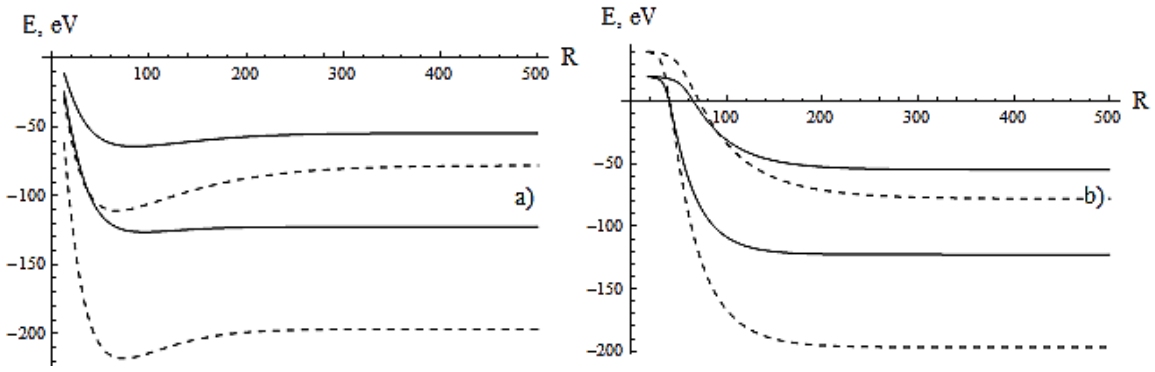


Fig. 4:The lowest levels of the two-electron atom (solid line) and of the one-electron atom (dotted line) with $Z = 2; 3$ as a function of cavity radius $R$ at $V_0 = 10\ eV$ for $d = a_B/4$ (a) and $d = 2a_B$ (b)

When $V_0 < 0$ the lowest level of the two-electron atom will always lies below the level of the corresponding one-electron atom. And for $V_{2el}^{crit}(Z) < V_0 < 0$ the lowest levels of the one- and two-electron atoms are exponential, and the ionization energy of the two-electron atomconverges rapidly with increasing $R$ to $E_{1el}(Z) - E_{2el}(Z)$. For $V_{1el}^{crit}(Z) < V_0 \leq V_{2el}^{crit}(Z)$ the lowest level of the two-electron atom is already power and the one of the one-electron atom is still exponential. In this case, the ionization energy of the two-electron atom converges slowly with increasing $R$ to $E_{1el}(Z) - \tilde{E}_{2el}(Z)$ as it is clearly shown in Fig. 5a for $V_0 = V_{2el}^{crit}(Z)$ and $d = a_B/4$. And for $V_0 \leq V_{1el}^{crit}(Z)$ both levels become power and the ionization energy slowly converges to $\tilde{E}_{1el}(Z)$ as it is shown in Fig. 5b for $V_0 = V_{1el}^{crit}(Z)$ and $d = a_B/4$.

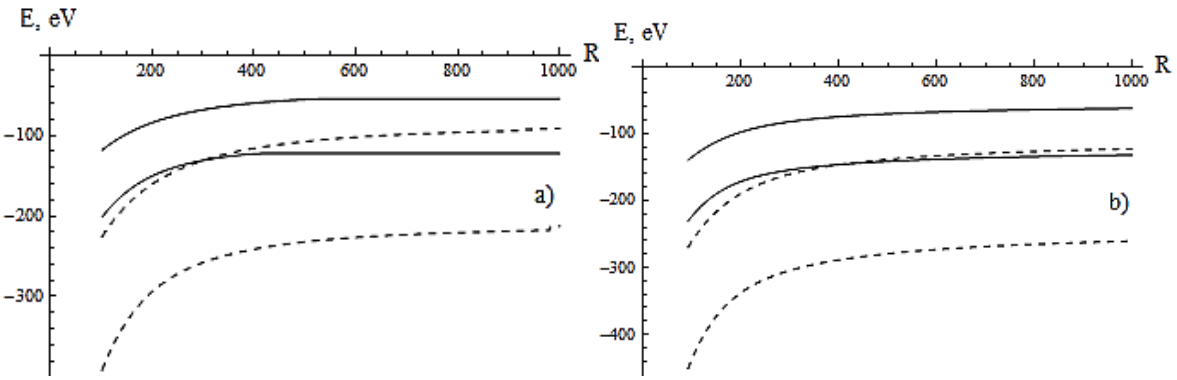


Fig. 5: The lowest levels of the two-electron atom (solid line) and of the one-electron atom (dotted line) with $Z = 2; 3$ as a function of cavity radius $R$ for $d = a_B/4$ at $V_0 = V_{2el}^{crit}(Z)$ (a) and $V_0 = V_{1el}^{crit}(Z)$ (b)

Thus, for $V_0 > 0$ there are always the outer shell parameters $V_0$, $R$ and $d$ that the two-electron atom in a cavity decays into the corresponding one-electron atom and an electron. On the other hand, there is such a set of the parameters that the binding and ionization energies of the two-electron atom in the cavity could be substantially bigger than the corresponding energies of the free one, and hence such a cavities are effective traps for the two-electron atoms.

## 5 CONCLUSIONS

To conclude it should be mentioned that the ansatz (8) is adequate for a qualitative studying the binding energy behavior of a two-electron atom in dependence on the cavity parameters for $Z \geq 2$. For $Z = 1$ in general the considered method is not sufficientlyaccurate even for qualitative studies. For example, in this approximation the ground state energy of the free two-electron atom with$Z = 1$lies above the ground state energy of the corresponding one-electron atom ($E_{2el}(Z = 1) \approx 0.95E_{1el}(Z = 1)$), so that one cannot even conclude that the free two-electron atom can be in the bound state. More precise calculations[30, 31] show that $E_{2el}(Z = 1) \approx 1.05E_{1el}(Z = 1)$. However, for the cavity parameters, for which the binding energy of the two-electron atom with$Z = 1$ is significantly bigger than the binding energy of the free one, the approximation (8) is quite adequate for the qualitative studying the behavior of the binding and ionization energies of the two-electron atom with $Z = 1$ in the cavity.

In the present work the behavior of the binding energy of the two-electron atoms in the cavity in dependence on parameters of potential, which confines the atomic electrons inside the cavity was studied. This potential is modeled in two ways: in the first case the electrons are confined inside the cavity by means of the $\delta$-shaped potential and in the second more realistic case by means of the outer potential shell of nonvanishing width with the boundary condition (18) imposed on the outer shell surface. It was shown that in both cases in dependence on the cavity parameters the two-electron atom in the cavity can decay into the corresponding one-electron atom and an electron or can be in the ground state, in which the binding and ionization energies are substantially bigger than the same energies of the free atom. The more realistic case with the outer potential shell is of specific interest because the boundary conditions (18) can provide not only the confinement of the electrons inside the cavity but also the periodic continuation of the wave function between neighboring cavities. As a result, such cavities could form the spatial lattice, as it occurs in the description of the metallic bond in the framework of the Wigner-Seitz model[21]. And in turn, for the certain cavity and shell parameters such a lattice could be an effective container for the two-electron atoms.

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