Spontaneous spherical symmetry breaking in atomic confinement

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The effect of spontaneous breaking of initial SO(3) symmetry is shown to be possible for an H-like atom in the ground state, when it is confined in a spherical box under general boundary conditions of “not going out” through the box surface (i.e. third kind or Robin’s ones), for a wide range of physically reasonable values of system parameters. The reason is that such boundary conditions could yield a large magnitude of electronic wavefunction in some sector of the box boundary, what in turn promotes atomic displacement from the box center towards this part of the boundary, and so the underlying SO(3) symmetry spontaneously breaks. The emerging Goldstone modes, coinciding with rotations around the box center, restore the symmetry by spreading the atom over a spherical shell localized at some distances from the box center. Atomic confinement inside the cavity proceeds dynamically — due to the boundary condition the deformation of electronic wavefunction near the boundary works as a spring, that returns the atomic nuclei back into the box volume.

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1. Introduction

The concept of broken symmetries is a cornerstone of such important physical effects as the Higgs mechanism in the electroweak sector of the standard model, confirmed recently by the discovery of corresponding boson, ferromagnetism, superconductivity and superfluidity. The common feature of all these phenomena is that they proceed in systems with infinite degrees of freedom like a phase transition with rise of nonzero quasi-average. As a result, the initial symmetry of the system reduces to a subgroup and an order parameter appears, which as a rule coincides with nonvanishing quasi-average. In systems with finite degrees of freedom, where field-theoretic/statistical nature is absent in principle, symmetry breaking doesn’t reveal such direct analogy with a phase transition. Nevertheless, in this case all the main features including nonzero quasi-average as well as Goldstone modes (in the case of broken continuous symmetry), which give rise to significant changes in the system properties, should exist at the same right.

The purpose of this letter is to explore such an effect, which takes place by confinement of atomic systems in a closed simply connected cavity. Such systems attract now considerable amount of theoretical and experimental activity [1]-[10], [13]-[22]. So far, starting from the works of Michels and de Boer [11], Sommerfeld and Welker [12], main attention has been devoted to the properties of atoms and molecules, confined by an impenetrable or partially penetrable potential wall ([1]-[4],[13]-[16] and refs. therein). However, actually general boundary conditions of “not going out” imply a quite different picture, where the particle WF doesn’t unavoidably vanish at the box boundary ([17]-[22] and refs. therein). As a consequence, the lowest energy levels of confined atomic system undergo a deep reconstruction, that might cause a spontaneous breakdown of the initial symmetry of the system. In particular, it occurs for atomic H placed in a spherical cavity, when for a wide range of physically reasonable values of system parameters a nonzero shift of atomic nuclei (the proton) from the center of cavity in the atomic ground state takes place, leading to broken rotational symmetry. In accordance with general features of broken symmetries, the shift is accompanied by emergence of corresponding Goldstone modes, representing fluctuations of spontaneous average under group transformations, in this case SO(3). In turn, these modes coincide with rotations around the cavity center and so restore the original symmetry, while atomic states acquire rotational quantum numbers and some additional nontrivial properties. Preliminary, but important results on this subject, motivated by the study of an endohedral atom in a fullerene cage [2],[5],[6], have been reported in ref. [23] a decade ago, where a simplified semi-analytic model, based on zero-range potential technique to mimic the interaction of an active electron with the residual atomic core, was considered, demonstrating the possibility of spontaneous SO(3) breakdown for strong attractive interaction. Here we present another approach to the problem starting from general “not going out” conditions, which allows for a detailed (quasi)exact study of the effect of rotational symmetry breaking not only for attractive, but for repulsive interaction too, as well as for various nontrivial asymptotical regimes.

It is worthwhile to note, that the general boundary conditions of “not going out” don’t unavoidably imply genuine trapping of a particle by a cavity, rather they could be caused by a wide range of reasons, as in the Wigner-Seitz model of alkaline metal [24], when the par-
ticle state is delocalized from the beginning. The latter circumstance turns out to be quite important, since in some cases the cavities, where a particle or an atom could reside, form a lattice, similar to that of an alkaline metal, like certain interstitial sites of a metal supercell, e.g., next-to-nearest octahedral positions of palladium fcc lattice [25]-[27]. In this case a particle (or valence atomic electron, provided that the whole lattice of cavities is occupied by atoms) finds itself in a periodic potential of a cubic lattice, and so on the boundary of corresponding Wigner-Seitz cell its ground state WF should be subject to Neumann condition (5), what is a special case of general “not going out” problem.

2. General treatment of a “not going out” state

The general approach to description of a “not going out” state for a particle in a vacuum cavity $\Omega$ with boundary $\Sigma$ starts with the following energy functional [17]-[21]

$$E[\psi] = \int_{\Omega} d\vec{r} \left[ \frac{\hbar^2}{2m} \nabla^2 \psi + U(\vec{r}) |\psi|^2 \right] +$$

$$+ \frac{\hbar^2}{2m} \int_{\Sigma} d\sigma \lambda(\vec{r}) |\psi|^2,$$  \hspace{1cm} (1)

where $U(\vec{r})$ is the potential inside $\Omega$, while the surface term $\int_{\Sigma}$ corresponds to contact interaction of particle with medium, in which the cavity has been formed, on its boundary. The properties of this surface interaction are given by a real-valued function $\lambda(\vec{r})$. A more realistic model of interaction with environment should imply the boundary in the form of a potential shell with definite magnitude and size [2], [5], [6], [20], but for our purposes it doesn’t play any significant role, since all the main effects of broken spherical symmetry show up already by contact interaction in (1).

From the variational principle with normalization condition $\langle \psi|\psi \rangle = \int_{\Omega} d\vec{r} |\psi|^2 = 1$ one obtains

$$\left[ -\frac{\hbar^2}{2m} \Delta + U(\vec{r}) \right] \psi = E\psi$$ \hspace{1cm} (2)

inside $\Omega$ combined with Robin’s (or third kind) boundary condition imposed on $\psi$ on the surface $\Sigma$

$$\left[ \vec{n}\nabla + \lambda(\vec{r}) \right] \psi_{\Sigma} = 0,$$ \hspace{1cm} (3)

with $\vec{n}$ being the outward normal to $\Sigma$. The “not going out” property is fulfilled here via vanishing normal to $\Sigma$ component of the quantum-mechanical flux

$$\vec{j} = \frac{\hbar}{2mi} \left( \psi^* \nabla \psi - \psi \nabla \psi^* \right)$$ \hspace{1cm} (4)

at the box boundary $\vec{n}\vec{j}|_{\Sigma} = 0$. At the same time, tangential components of $\vec{j}$ could be remarkably different from zero on $\Sigma$ and so the particle could be found quite close to the boundary with a marked probability. Such a picture is similar to that of the Thomas-Fermi model of many-electron atom [28], as well as to quark bag models of hadron physics [29],[30].

For a spherical cavity the spectral problem (2-3) is self-adjoint and so contains all the required properties for a correct quantum-mechanical description of a non-relativistic particle confined in $\Omega$. For a more complicated geometry the set of requirements to $\Omega$ and $\Sigma$, under which the problem (2-3) allows for a self-consistent treatment, is discussed in [18],[19],[21].

When $\lambda = 0$, interaction of the particle with environment is absent and so eq. (3) transforms into Neumann (second kind) condition

$$\vec{n} \nabla \psi |_{\Sigma} = 0,$$ \hspace{1cm} (5)

what is similar to the boundary condition of confinement for a scalar field in relativistic bag models [29]. Moreover, condition (5) appears in the Wigner-Seitz model of an alkaline metal [24] and describes an opposite picture, namely delocalization of valence electrons creating the metallic bond, by continuing the electronic WF periodically in the lattice. So the “not going out” state with Neumann condition turns out to be of special interest, since in media with long-range order such vacuum cavities could form a (sub)lattice [25]-[27]. Let us also mention, that in the case of atomic H the condition (5) is nothing else, but the boundary condition for the Wigner-Seitz cell in hypothetical metallic atomic phase (see e.g. [31] and refs. therein), which should be the simplest alkaline metal.

If $\lambda \to \infty$, then (3) turns into Dirichlet condition

$$\psi_{\Sigma} = 0,$$ \hspace{1cm} (6)

and so describes confinement by an impenetrable barrier. However, when $\lambda \to -\infty$, the answer depends on the size of cavity. When the latter is finite, the atomic position in the center of cavity becomes unstable and the atom sticks to the boundary, whereas if the cavity size grows infinitely, the curvature of the boundary becomes negligibly small and there appears a separate nontrivial problem of atomic states over a plane with boundary condition (3), whose solution depends strongly on concrete relation between $\lambda$ and atomic nuclei charge $q$ (for a more detailed discussion of the latter problem see Section 4).

3. Atomic H in the center of cavity

The problem under consideration concerns atomic H with nuclei charge $q$ in a spherical cavity with size $R$ and boundary condition (3), when the surface interaction is given by a constant $\lambda$ and so the system reveals spherical symmetry. Besides [23], most of works on this subject starting from [11], [12] till nowadays [1]-[4],[13]-[22], propose that the atomic nuclei should reside in the center of
cavity. Then spherical symmetry is maintained and the radial electronic WF with orbital momentum \( l \) up to a numerical factor takes the following form [28] 
\[
R_l(r) = e^{-\gamma r} r^l \Phi(b_l, c_l, 2\gamma r) ,
\]
where 
\[
\gamma = \sqrt{-2E} , \quad b_l = l + 1 - q/\gamma , \quad c_l = 2l + 2 ,
\]
and \( \Phi(b, c, z) \) is the first kind confluent hypergeometric (Kummer) function. Definition, notations and main properties of the Kummer function follow ref. [32]. In what follows, in order to provide an effective comparison of results obtained previously, universal relativistic units \( h = c = 1 \) are used, wavenumber and energy are expressed in units of the electron mass \( m \), while distances — in units of corresponding Compton length \( 1/m \), and e-m coupling constant \( \alpha \) is included in the nuclei charge \( q = Z \alpha \). Such units are in particular quite convenient for accounting of relativistic effects as well as for numerical calculations in the Schroedinger case, since step one in Compton length units corresponds to the continuous limit of nonrelativistic problem.

Substituting (7) into the boundary condition (3) yields the following equation for energy levels 
\[
[q/\gamma + (\lambda - \gamma) R - 1] \Phi_R + [l + 1 - q/\gamma] \Phi_R(b+) = 0 ,
\]
where 
\[
\Phi_R = \Phi(b_l, c_l, 2\gamma R) , \quad \Phi_R(b+) = \Phi(b_l+1, c_l, 2\gamma R) .
\]

There are the following properties of electronic levels for an H-like atom in the center of cavity, that are of interest for further analysis. The most significant changes in the spectrum take place for \( R \to 0 \). Here it should be noted, that for atomic H the limit \( R \to 0 \) requires some care, since relativistic effects give rise to the restriction \( R \geq 10 \) for the cavity sizes, where such an approach to the confinement problem, based on boundary condition (3), should be valid [20]. So in what follows the limit \( R \to 0 \) should be understood either as a purely mathematical property of equations under consideration, or as decreasing \( R \) up to \( R \sim 10 \).

There are two types of lowest levels for atomic H in dependence on relation between \( \lambda \) and \( q \). The first one takes place under assumption, that for \( R \to 0 \) the wavenumber \( \gamma \) remains finite, and so in the vicinity of \( R = 0 \) it could be represented by a series 
\[
\gamma(R) = \gamma_0 + \gamma_1 R + \gamma_2 R^2 + \ldots .
\]
Expanding \( \Phi_R , \Phi_R(b+) \) as a power series in \( R \), to the lowest order one obtains from (9) that \( l = 0 \), and by proceeding further 
\[
\lambda = q , \quad \gamma_0 = q^2 , \quad \gamma_n = 0 , \quad n \geq 1 .
\]
From (12) there follows the result, already mentioned in [17],[18], that when \( \lambda = q \), then the ground state energy of atomic H in a cavity for any \( 0 < R \leq \infty \) precisely coincides with that of 1s-level of the free atom
\[
E_{ground}(R) = E_{1s} = -q^2/2 ,
\]
while the electronic WF coincides inside the cavity with corresponding one of free H.

Another type of levels is found by assumption, that in the vicinity of \( R = 0 \) the wavenumber \( \gamma \) is represented by a series 
\[
\gamma(R) = \frac{\xi}{\sqrt{R}} + \xi_0 + \xi_1 \sqrt{R} + \ldots .
\]
Substituting (14) into eq. (9), to the lowest order in \( \sqrt{R} \) one obtains again \( l = 0 \), while higher orders of expansion in \( \sqrt{R} \) yield 
\[
\xi^2 = 3(q-\lambda) , \quad \xi_0 = 0 , \quad \xi_1 = \frac{q^2 + 3q\lambda + 6\lambda^2}{20\xi} , \quad \ldots .
\]
As a result, for such type of s-levels in a cavity one obtains the following dependence on the cavity size for \( R \to 0 \)
\[
E_{ground}(R) \to \frac{3(q-\lambda)}{2R} - \frac{q^2 + 3q\lambda + 6\lambda^2}{20} + O(\sqrt{R}) ,
\]
\[
R \to 0 ,
\]
what coincides with (13) for \( \lambda = q \).

Qualitative explanation of linear dependence on \( q \) and \( \lambda \) in (16) is quite simple. As for a particle in a spherical well [19],[20], for \( R \to 0 \) the electronic WF of such 1s-level inside a cavity becomes almost constant, and substitution of corresponding normalization constant into (1) yields immediately the leading term in the asymptotics (16).

The peculiar features of the problem (2-3) show up for \( R \to \infty \) as well, when it could be found via asymptotic expansion for \( \Phi_R , \Phi_R(b+) \) in (9), that in the case of surface attraction \( \lambda < 0 \) there exists besides the discrete spectrum of the free atom one more level \( E(R) \) with negative limiting value \( E(\infty) = -\lambda^2/2 \) and power behavior for \( R \to \infty \)
\[
E(R) \to -\lambda^2/2 - (q-\lambda)/R + O(1/R^2) , \quad R \to \infty .
\]
For \( \lambda < -q < 0 \) such a power level \( \tilde{E}(R) \) turns out to be the lowest electronic s-level for all \( R \) and looks like a shifted downwards hyperbole, as for a particle in a well [17],[20].

At the same time, the levels originating from the discrete spectrum of free H, tend for \( R \to \infty \) to their asymptotical values, corresponding to those of free H, exponentially fast [17],[18],[20]. Moreover, for atomic H in a spherical box the Runge-Lenz vector isn’t conserved yet [19],[22], hence these levels should be labeled with two
quantum numbers \( n = n_r + 1 \) and \( l \). In particular, for the \( ns\)-levels one finds

\[
E_n(R) - E_n \to \left[ \frac{\gamma_n}{n!} \right]^2 \frac{\lambda - \gamma_n}{\lambda + \gamma_n} (2\gamma_n R)^{2n} e^{-2\gamma_n R},
\]

\[\gamma_n R \gg 1,\]

where

\[E_n = -\frac{\gamma_n^2}{2}, \quad \gamma_n = q/n, \quad n = 1, 2, \ldots,\]

are the electronic \( ns\)-levels of the free atom. Remark, that levels with \( \gamma_n < \lambda \) should approach their asymptotics from above, while those with \( \gamma_n > \lambda \) from below.

It should be specially noted, that the asymptotics (18) turns out to be an exceptional feature of those confined atom electronic levels, which originate from the discrete spectrum of the free atom, since such asymptotics is created by approaching the argument of the factor \( \Gamma^{-1}(b) \), entering the asymptotics of the Kummer function \( \Phi(b, c, z) \), to the pole \( b \to -n_r \), \( n_r = 0, 1, \ldots \). Asymptotics for \( R \to \infty \) of all the other electronic levels in a cavity, which originate from the continuous spectrum of the free atom, and of the additional powerlike level (17), caused by attractive interaction with environment, turns out to be a power series in \( 1/R \), and their asymptotical values could be either non-negative only, or for \( \lambda < 0 \) contain one negative point \( E(\infty) = -\lambda^2/2 \) [20].

For \( \lambda = \pm \gamma_n \) the asymptotics (18) modifies in the next way. The exponential behavior is preserved, while the non-exponential factor undergoes changes in such a way, that the \( ns\)-levels approach their asymptotics of the free atom from above only. For \( \lambda = \gamma_n > 0 \) their asymptotics takes the form

\[
E_n(R) - E_n \to (n - 1) \left[ \frac{\gamma_n}{n!} \right]^2 (2\gamma_n R)^{2(n-1)} e^{-2\gamma_n R},
\]

\[\gamma_n R \gg 1,\]

while for the lowest level \( E_1(R) \) the exponential part disappears completely, since in this case \( \lambda = \gamma_1 = q \), and as it was mentioned above, \( E_1(R) \) becomes a constant, which coincides with \( E_{1s} = -q^2/2 \).

For \( \lambda = -\gamma_n < 0 \) instead of (18) one obtains

\[
E_n(R) - E_n \to \frac{1}{n + 1} \left[ \frac{\gamma_n}{n!} \right]^2 (2\gamma_n R)^{2(n+1)} e^{-2\gamma_n R},
\]

\[\gamma_n R \gg 1,\]

and moreover, the limiting point \( \tilde{E}(\infty) \) of the level \( \tilde{E}(R) \) with the power asymptotics (17) coincides with the corresponding level \( E_n \) of the free atom (19), what in turn represents a remarkable example of von Neumann-Wigner avoiding crossing effect, i.e. near levels reflection under perturbation [28],[33] — infinitely close to each other for \( R \to \infty \) levels \( E_n(R) \) and \( \tilde{E}(R) \) should for decreasing \( R \) diverge in opposite directions from their common limiting point \( E_n \). Perturbation in this case is performed by the atomic nuclei Coulomb field, since under general boundary conditions (3) the electronic WF doesn’t vanish on the cavity boundary, and so for \( R > 1 \) the maximum of electronic density should be shifted into the region of large distances between the electron and nuclei, where the contribution of the Coulomb field is negligible compared to boundary effects. When \( R \) decreases, the Coulomb field increases, hence \( E_n(R) \) should go upwards according to (21), while \( \tilde{E}(R) \) goes downwards according to the asymptotics

\[\tilde{E}(R) \to E_n - \frac{n+1}{n} \frac{q}{R} + O(1/R^2), \quad R \to \infty.\]  

So the lowest electronic level of atomic H, confined in a cavity with Robin’s condition (3), turns out to be the following [17],[18],[20]. For \( \lambda = q \) it acquires the constant value \( E_{1s} \) of the free atom, for \( \lambda > -q \) behaves for \( R \to 0 \) according to (16) with an energy shift depending on \( \lambda \) and for \( R \to \infty \) it approaches \( E_{1s} \) exponentially fast, while for \( \lambda > -q < 0 \) transforms into the level \( \tilde{E}(R) \) with power asymptotics (17).

4. The machinery of spherical symmetry breaking for atomic “not going out” state

Actually the assumption of spherical symmetry of the atomic ground state in a spherical box doesn’t hold for \( \lambda < q \). The reason is that for boundary conditions (3) electronic WF could be localized in the vicinity of the cavity boundary, hence the most favorable atomic configuration should be that one, when the atomic nuclei is shifted from the center of cavity. What is here the most nontrivial, that while for \( \lambda < 0 \) the atomic displacement turns out to be an almost obvious consequence of electron attraction to the cavity boundary, for \( \lambda > 0 \), i.e. for electron reflection from the boundary, the emerging asymmetric distortion of electronic WF could yield an energy decrease as well. Moreover, there appears a quite complicated dependence on the cavity size. The crucial role in this effect is played by the boundary condition (3). The fine structure and other spin effects turn out to be negligibly small compared to those coming from the boundary condition and so are neglected in what follows.

As a first step let us consider this effect via special kind trial function. For these purposes the coordinate frame with origin in the cavity center turns out to be the most convenient. Assuming that the adiabatic approximation is valid, for atomic nuclei placed in the point \( \vec{a} = (0,0,a) \) the electronic hamiltonian takes the form (in what follows the genuine atomic H with \( Z = 1 \) is considered, hence \( q = a \))

\[H_{el} = -\frac{1}{2} \Delta \phi - \frac{\alpha}{|\vec{r} - \vec{a}|}.\]  

(23)
The trial function is chosen as a superposition of \(N\) first angular harmonics with zero momentum projection on \(z\)-axis (rotation over \(z\)-axis maintains the symmetry, so \(l_z\) remains an actual quantum number, while the energy eigenvalue is minimized for \(l_z = 0\))

\[
\Psi_{tr}(r, \theta) = \sum_{l=0}^{N} c_l \ R_l(r) \ P_l(\cos \theta) , \tag{24}
\]

and with radial functions of the structure similar to that of lowest \(H\)-levels with momentum \(l\)

\[
R_l(r) = d_l \ r^l e^{-\gamma_l r} . \tag{25}
\]

The variation parameters are here the coefficients \(c_l\), which could be taken real from the beginning, while \(\gamma_l, d_l\) are determined via boundary condition and normalization of \(\Psi_{tr}\)

\[
\gamma_l = \lambda + \frac{l}{R} , \quad d_l = \left( \frac{2l + 1}{4\pi} \ \frac{(2\gamma_l)^{2l+3}}{\Gamma(2l + 3, 0, 2\gamma_l R)} \right)^{1/2} , \tag{26}
\]

with \(\Gamma(z, x_0, x_1) = \int_{x_0}^{x_1} t^{z-1} e^{-t} dt\) being the generalized incomplete gamma-function. With \(\gamma_l\) taken in the form (26) such a trial function fulfills exactly the boundary condition (3), and so a nonzero displacement shows up already for \(\lambda > 0\).

The normalization of the trial function takes the form

\[
\langle \Psi_{tr} | \Psi_{tr} \rangle = \sum_{l=0}^{N} c_l^2 , \tag{27}
\]

while for the energy functional (1) one obtains the following quadratic form in \(c_l\)

\[
E[\Psi_{tr}] = \langle \Psi_{tr}|H|\Psi_{tr}\rangle = \sum_{l=0}^{N} c_l A_{ls} c_s , \tag{28}
\]

where

\[
A_{ls} = (K_l + \lambda B_l) \delta_{ls} - 2\alpha V_{ls} . \tag{29}
\]

In the matrix \(A_{ls}\) the diagonal kinetic \(K_l\) and surface \(B_l\) terms can be written as

\[
K_l = \frac{d_l^2}{(2l + 1)(2\gamma_l)^{2l+1}} \left[ \frac{1}{4} \Gamma(2l + 3, 0, 2\gamma_l R) - \right.

\left. - l\Gamma(2l + 2, 0, 2\gamma_l R) + (2l + 1)\Gamma(2l + 1, 0, 2\gamma_l R) \right] , \tag{30}
\]

\[
B_l = \frac{d_l^2}{(2l + 1)} \ R^{2l+2} e^{-2\gamma_l R} , \tag{31}
\]

while for the Coulomb interaction the terms \(V_{ls}\)

\[
V_{ls} = \sum_{k=|l-s|}^{l+s} W_{lsk}(a) \left( \begin{array}{c} l \ s \ k \\ 0 \ 0 \ 0 \end{array} \right)^2 , \tag{32}
\]

where

\[
W_{lsk}(a) = d_l \ \frac{\Gamma(l + s + k + 3, 0, (\gamma_l + \gamma_s) a)}{a^{k+1}(\gamma_l + \gamma_s)^{l+s+k+3}} + \right. \nonumber

\left. + a^{k} \ \frac{\Gamma(l + s - k + 2, (\gamma_l + \gamma_s) a, (\gamma_l + \gamma_s) R)}{(\gamma_l + \gamma_s)^{l+s-k+2}} \right) \ d_s , \tag{33}
\]

are responding.

\(E_{tr}\) is determined from the variational problem for \(c_l\) via secular equation

\[
\det |A_{ls} - E_{tr} \delta_{ls}| = 0 , \tag{34}
\]

which could be easily solved by means of standard numerical recipes. The resulting dependence \(E_{tr}(a)\), obtained for \(N = 10\), is shown on Fig.1 The minimum on the curve \(E_{tr}(a)\) depends strongly on actual values of \(\lambda\) and \(R\). Tab.1 shows the relation between the energy \(E_0(0)\) of unshifted \(H\) lowest level, calculated from (9), and the minimal value \(E_{tr}(a_{min})\) found for \(E_{tr}(a)\).

\[
|E, eV|
\begin{array}{|c|c|c|c|c|c|c|c|c|}
\hline
\lambda/\alpha & 0.5 & 0 & -0.5 & -1.0 & -1.5 & 200 & 400 & 600 & 800 & 1000 & 1200 & 1400 \\
\hline
-0.473 & -0.388 & -1.669 & -2.839 & -3.279 & -3.632 & -3.362 & -1.963 & -5.12 & -0.843 & -1.963 & -6.505 & -13.998 & -14.822 \\
0.1425 & 4.673 & 4.005 & 2.169 & 0.512 & -0.843 & -1.963 & -5.12 & -0.843 & -1.963 & -6.505 & -13.998 & -14.822 \\
-0.530 & 11.312 & 12.968 & 12.078 & 9.977 & 8.086 & 6.505 & -13.998 & -14.822 \\
-1.0 & 8.001 & 16.233 & 17.719 & 17.241 & 15.082 & 13.998 & -14.822 \\
-1.5 & 11.221 & 19.188 & 19.890 & 18.887 & 17.494 & 16.1 & -14.822 \\
\hline
\end{array}
\]

Tab.1. The values of \(\Delta E = E_0(0) - E_{tr}(a_{min})\), given in eV, for \(R = 200 - 1400\) and 5 values of \(\lambda/\alpha\) from the range \(-1.5 \leq \lambda/\alpha \leq 0.5\).

So in the trial function approximation (24) there is no effect for \(\lambda/\alpha = 0.5\) and any \(R\) from the range considered above, while for other \(\lambda\) the shift is already present, but the dependence of the depth of shifted minimum on \(R\) isn’t monotonic — the mostly pronounced effect is achieved for \(400 < R < 600\).
(Quasi)exact analysis of atomic displacement is performed numerically on the basis of the following algorithm. Let us pass to the coordinate frame with origin in the proton. Assuming that the proton shift from cavity center is \( a \) in Oz direction, for the distance \( R_{\Sigma} \) between the proton and cavity boundary one finds the following dependence on the polar angle \( \theta \)

\[
r_{\Sigma}(\theta) = \sqrt{R^2 - a^2 \sin^2 \theta} - a \cos \theta ,
\]

(35)

operator \( n\nabla \big|_{\Sigma} \) in the proton rest frame takes the form

\[
\big|_{\Sigma} n\nabla = \left( A \frac{\partial}{\partial r} + B \frac{\partial}{\partial \theta} \right) |_{r=r_{\Sigma}} ,
\]

(36)

where

\[
A = \frac{\sqrt{R^2 - a^2 \sin^2 \theta}}{R} , \quad B = -\frac{a \sin \theta}{R \ r_{\Sigma}(\theta)} .
\]

(37)

The ground state electronic WF is assumed to be of the form (24) with \( R_i(r) \) being now the radial Coulomb functions (7-8), while coefficients \( q_i \) are determined from the boundary condition (3), what leads to secular equation for the energy levels of the form

\[
\det I = 0 ,
\]

(38)

where

\[
I_{ts} = \int_{-1}^{1} dx \left[ (AR_t^i + \lambda R_t^i) P_t(x) + BR_t P_t^1(x) \right]_{r=r_{\Sigma}} P_s(x) .
\]

(39)

In (39) the argument of Kummer function is \( r_{\Sigma} \) (35), where \( \cos \theta = x \), thence the integral in (39) cannot be calculated analytically, but allows for a detailed numerical analysis. For \( 100 < R < 1000 \) the precision of order 0.01 eV for the lowest level is achieved for \( N \geq 12 \). Check-up of calculations based on (38-39) is performed by means of direct solution of initial Schrödinger eq. with hamiltonian (23) via shooting from the cavity center into boundary condition with such a number of harmonics, that provides relative error to be not more than 5%. For these purposes 18-36 angular harmonics are used, while for calculations based on (38-39) their number is 12-16, but in the latter case there appears an additional problem with controlling the required precision in (39), since it contains integration of oscillating functions with very large, exceeding several orders in magnitude, jumps of amplitudes, what requires application of arbitrary-precision (bignum) arithmetics.

The typical behavior of the lowest electronic energy \( E_0(a) \) compared to the estimate via trial function (24) is shown on Fig.2. On the whole, it reproduces the result obtained by means of (24), but now the displacement effect takes place for sufficiently more large \( \lambda > 0 \), while the well, where the energy is minimized, turns out to be much deeper with a pronounced barrier for \( a \to R \), which emerges due to significant increase of deformation, hence of gradients, in electronic WF, when the proton approaches the box boundary.

Phase diagram for regions of existence and absence of the displacement effect in parametrization \( \lambda/\alpha \), \( R \) is shown on Fig.3. The boundary curve between these regions is determined from relation \( \partial E_0(a)/\partial a = 0 \) for \( a \to 0 \) and henceforth is marked as \( \lambda^*(R) \) or \( R^*(\lambda) \). The displacement effect is always absent for \( \lambda \geq \alpha \), what is a direct consequence of that for the lowest electronic state in a cavity with boundary condition (3) for \( \lambda = \alpha \) and any \( R \) there exists the exact solution (13) with \( H \) placed in the center, which coincides with 1s-level of the free atom. For larger \( \lambda \) the reflection from the boundary becomes even greater uniformly in all directions, hence \( H \) remains in the cavity center. For \( \lambda < \alpha \) the atomic displacement depends on relation between \( \lambda \) and \( \lambda^*(R) \). When \( \lambda < \lambda^*(R) \), a nonzero displacement becomes an immanent feature of atomic ground state, the more pronounced, the smaller the ratio \( \lambda/\lambda^* \) turns out to be.

The dependence of the shifted electronic energy minimum \( E_{\min} = E_0(a_{\min}) \) on \( \lambda/\alpha \) for cavity sizes from the range \( 100 < R < 1000 \) is shown on Fig.4. Fig.5 repre-
appears a marked deformation of electronic WF and the displacement effect grows rapidly. For $R \gg R^*$ there appears another effect — since the boundary curvature becomes small, the displacement tends to the asymptotic regime of an H “soaring” over a plane at some height, defined by actual values of $q$ and $\lambda$.

By itself the problem of an H-like atom “soaring” over a plane with boundary condition (3) requires a separate and highly nontrivial analysis, since in this case an interplay between two different symmetries — spherical Coulomb and the axial one, caused by the boundary condition on a plane, takes place. Therefore the problem requires quite different methods of analysis and won’t be discussed here in detail. Here only a brief sketch of most important features of this problem, which are necessary for correct interpretation of results for a box of extremely large size, will be presented. Firstly, for $\lambda \geq q$ a sufficiently strong reflection, which pushes H infinitely far from the plane, takes place. This is because for such $\lambda$ and any finite $R$ the atom resides in the cavity center. It should be noted, that already this effect is nontrivial, since an infinite atomic jump away from the plane takes place for finite $\lambda \geq q$. On the contrary, for $\lambda < q$ the energy of the lowest electronic level is minimized at finite distances $d$ between them. This statement could be verified via following variational estimate. Let us pass to the cylindrical coordinates $(\rho, \varphi, z)$, when the lowest level WF takes the form $\psi(\rho, z)$, the position of atomic nuclei over a plane $z = 0$ is given by $\vec{d} = (0, 0, d)$, while the corresponding energy functional is written as

$$E[\psi] = \int_0^{\infty} dz \int d\rho d\varphi \left[ \frac{l}{2} |\nabla \psi|^2 + U(\rho, z) |\psi|^2 \right] + \frac{\lambda}{2} \int d\rho |\psi(\rho, 0)|^2 ,$$

where

$$U(\rho, z) = -q/\sqrt{\rho^2 + (z - d)^2} .$$

![FIG. 4: The dependence of the shifted energy minimum $E_{\text{min}} = E_0(a_{\text{min}})$ on $\lambda/\alpha$.](image1)

![FIG. 5: The dependence of the parameter $x = a_{\text{min}}/R$ for the energy minimum on $\lambda/\alpha$.](image2)

![FIG. 6: The dependence of the parameter $1 - x = (R - a_{\text{min}})/R$ for the energy minimum on $\lambda/\alpha$.](image3)
The pertinent trial function is chosen in the form

$$\Psi_{tr}(\rho, z) = C \exp \left[ -A\sqrt{\rho^2 + (z-d)^2} - B(z-d) \right] ,$$

(42)

with $C$ being the normalization factor, while $A, B$ are the variational parameters. To establish the existence of a nontrivial minimum in $E_0(d)$ for finite $d$ and $\lambda < q$, it suffices to deal with fixed values of parameters $A = 1$, $B = 0$ without exploring the variational procedure for their definition. In this case one obtains from (40) for the estimate of the lowest level energy

$$E[\Psi_{tr}] = -\frac{q^2}{2} - e^{-2qd}(1 + 2\lambda d + \lambda/q - qd)/2$$

(43)

$$\frac{1}{1 - e^{-2qd}(1 + qd)/2}.$$ 

Now let $qd \gg 1$, what means actually that $d \gg a_B$. Then it is possible to represent (43) as a series in powers of $\exp(-2qd)$, what leads to the following result for $E_{tr}$

$$E_{tr} = -\frac{q^2}{2} + e^{-2qd}[\lambda/q + 2qd(\lambda/q - 1)] + O(e^{-qd}) .$$

(44)

At this stage we recall the results of the preceding section, that $E_0(d \to \infty) = -q^2/2$ for $\lambda > -q$ and $E_0(d \to \infty) = -\lambda^2/2$ for $\lambda < -q$. Proceeding further, from (44) one finds, that when $|\lambda/q| < 1$, there holds for sufficiently large $qd$, that $E_{tr} < -q^2/2$, i.e. for the trial function of the form (42) $E_{tr}$ turns out to be smaller, than the exact value of electronic energy for infinite distance between the atom and plane. So the minimal energy of the electronic level is achieved in this case for (possibly quite large), but definitely finite distance between the atom and plane. At the same time, for $\lambda < -q$ this effect should be even stronger, since the electronic attraction to the plane increases. The circumstance, that the function (42) doesn’t satisfy the boundary condition (3), which takes now the form

$$\frac{\partial}{\partial z} \psi(\rho, z)\big|_{z=0} = 0 ,$$

(45)

cannot pose any problems for the status of the estimate considered above. The reason is that (3) and (45) appear as additional equations within the variational problem for energy functionals (1, 40), caused by restrictions on the integration region, and so should be satisfied only by the exact solution, corresponding to the true energy minimum, while $E_{tr}$, obtained from (40) via integration over the same region $z \geq 0$, turns out to be a correct estimate for exact minimum of the functional (40) from above.

By means of (44) it is also possible to estimate the distance from the plane via position of the minimum of $E_{tr}(d)$

$$d_{min} = \frac{1}{2(1 - \lambda/q)} .$$

(46)

Here it should be noted once more, that formulae (44) and (46) can be used as estimates for the position of electronic energy minimum for sufficiently large $d$ and correspondingly $d_{min}$ only. Actually they could be remarkably different from the true energy minimum, since the parameters $A$ and $B$ in the trial function (42) are chosen in the simplest way, ignoring the variational procedure, just in order to establish the fact of attraction between the atom and plane for $\lambda < q$. Nevertheless, as the (quasi)exact numerical solution shows, these estimates agree quite well with the true minimum, whenever the latter is reached at sufficiently large distance between the atom and plane.

The results of numerical calculations of correct values for the electronic energy minimum of atomic H over a plane, obtained via gradient descent method, are shown in Tab.2.

| $\lambda/q$ | $d_{min}$ | $E_{min}$ |
|-----------|-----------|-----------|
| 0.8       | 324.7     | -13.61    |
| 0.6       | 158.6     | -13.90    |
| 0.3       | 86.0      | -15.45    |
| 0.0       | 57.3      | -18.47    |
| -0.3      | 42.3      | -23.20    |
| -0.6      | 33.4      | -29.68    |
| -1.2      | 23.3      | -48.72    |

Tab.2. (Quasi)exact values for the position and value (in eV) of the energy minimum for the lowest electronic level of atomic H over a plane.

First line in Tab.2 shows, that the minimum of electronic energy of atomic H for $\lambda = 0.8a$ lies sufficiently far from the plane --- $d_{min} \simeq 2.37a_B$, and so agrees quite well with estimate (46) presented above, which gives in this case for $d_{min}$ the value $\simeq 2.5a_B$.

Now let us present (quasi)exact numerical results for the behavior of atomic H in a cavity of large size $R$, which show explicitly, how it approaches the asymptotical regime of “soaring” over a plane. Figs. 7-9 demonstrate the dependence on $R$ of the bound energy and displacement for the lowest electronic level in the range $-1.2 \leq R/\lambda \leq 0.8$. It should be specially noted, that for $\lambda = 0.8a \simeq \lambda^* \simeq \lambda^*$ the displacement effect presented on Figs. 7,8 shows up very weakly (see Fig.10 below too), since it takes place only in cavities with $R > R^* \gg a_B$, when the displacement itself turns out to be quite large too, while the decrease of the level energy is very small. Therefore for such $\lambda$ an enhanced precision by calculation of the effect is required, what is achieved via smooth extrapolation of contributions of angular harmonics from the range 20-30-40-50 to more large values, that allows in turn for a correct account of contribution from higher orbital momenta up to $l \sim 100 - 200$ and even more.

On Fig. 7 the curves for the electronic bound energy as a function of $R$ are shown, Fig.8 represents the dependence on $R$ for the relative displacement in units of $R$ of the energy minimum $x = a_{min}/R$ for the same $\lambda/\alpha$, while Fig.9 displays the distance between the box boundary and the position of the energy minimum $d_{min} = R - a_{min}$. On the contrary to Figs. 7,8,
each curve shown on Fig.9 contains a minimum for finite $R$ from the range $100 < R < 1000$, which is well pronounced for $\lambda = 0.8\alpha \approx \lambda^*$, but for decreasing $\lambda$, hence for increasing attraction to the boundary, becomes rapidly very weak. The reason is that for such box sizes the distance between the atom and the box boundary approaches its asymptotical value corresponding to the atomic “soaring” over a plane more and more quickly, while for $\lambda = 0.8\alpha \approx \lambda^*$ in the range $100 < R < 1000$ this effect isn’t present yet.

A comparison of results for a box of a large size $R = 7a_B \approx 1000$ and for a plane with $R = \infty$ is given in Tab.3, which confirms the result quoted above — with growing $\lambda/q$ a more and more large $R$ is required for approaching the asymptotical regime.

| $\lambda/q$ | $d_{\text{min}}(\infty)$ | $d_{\text{min}}(7a_B)$ | $E_{\text{min}}(\infty)$ | $E_{\text{min}}(7a_B)$ |
|-------------|---------------------------|------------------------|--------------------------|------------------------|
| 0.8         | 324.7                     | 253.5                  | -13.61                   | -13.68                 |
| 0.6         | 158.6                     | 141.4                  | -13.90                   | -14.23                 |
| 0.3         | 86.0                      | 81.5                   | -15.45                   | -16.37                 |
| 0.0         | 57.3                      | 55.8                   | -18.47                   | -20.18                 |
| -0.3        | 42.3                      | 41.8                   | -23.20                   | -25.81                 |
| -0.6        | 33.4                      | 33.3                   | -29.68                   | -33.32                 |
| -1.2        | 23.3                      | 23.3                   | -48.72                   | -54.48                 |

Tab.3. The position and magnitude (in eV) of the energy minimum for the lowest electronic level of atomic H over a plane ($R = \infty$) and for a cavity of a large radius ($R = 7a_B$).

5. Atomic H ground state shifted from the center of cavity

Now let us turn to the dynamics of atomic H as a whole by treating the position of atomic nuclei $\vec{a}$ as a dynamical variable. The dynamics of nuclei restores the broken by atomic displacement initial $SO(3)$ via rotations of the shifted atom around the cavity center, whereas angular components of $\vec{a}$ serve as Goldstone modes, which describe fluctuations of spontaneous average (atomic displacement) under $SO(3)$ group transformations.

Within adiabatic approximation the corresponding effective hamiltonian for the dynamics of atomic nuclei takes the form

$$H_{\text{eff}} = \frac{1}{2M} \Delta \vec{a} + E_0(a) + E_{\text{rec}}(a),$$

with $M$ being the nuclei (proton) mass, $E_0(a)$ is the lowest electronic level, considered in detail in the preceding section, while $E_{\text{rec}}(a)$ is a specific effect, analogous to the recoil effect for the free atom, when a correction

$$\Delta E_{\text{rec}} = \frac{m}{M} \frac{\vec{p}^2}{2m_{\text{el}}}$$

appears. In the case under consideration $E_{\text{rec}}(a)$ is caused by nuclei back-reaction on the electronic WF de-
formation and takes the same form
\[ E_{rec}(a) = \frac{1}{2M} \langle \psi_{el} | \vec{P}_{sol}^2 | \psi_{el} \rangle \]  
(49)
with that crucial difference, that now \( \vec{p}_a = -i \vec{\nabla}_a \) doesn’t possess the status of spatial translations generator for the electronic \( \psi_{el}(\vec{r}, \vec{a}) \), rather it defines the “kinetic” effect of electronic WF distortion caused by atomic displacement. The most consistent way to derive the expression (49) is based on field quantization in the vicinity of a boson soliton by means of collective (group) variables (see [34]-[36] and refs. therein). In the case under consideration the role of bosonic soliton is played by the atomic nuclei with Coulomb field, while the electronic state appears as one-particle excitation in the Furry picture for fermion (electron-positron) field, that is considered in soliton background at the same footing with secondly quantized bosonic component. For a translationally invariant system, when the total momentum is conserved, the kinetic energy operator to the leading order of expansion in inverse powers of soliton mass takes the form [35],[36]
\[ E_{kin} = \frac{1}{2M} \left[ \vec{P}^2 + \int d\vec{r} \vec{\nabla} \Phi \Pi + : \int d\vec{r} \chi^+ i \vec{\nabla} \chi : \right] , \]  
(50)
with \( M \) being the soliton (atomic nuclei) mass, \( \vec{P} \) is the total momentum, while \( \Phi, \Pi \) and \( \chi^+, \chi \) denote the secondly quantized boson field and its canonically conjugated momentum and the fermion field in the soliton rest frame. The normal ordering in (50) provides the validity of condition, that in the plane-wave basis for \( \Phi \) and \( \chi \) the kinetic energy of one-particle state with momentum \( \vec{k} \) should be of the form
\[ E_{kin} = \left( \vec{P} - \vec{k} \right)^2 /2M = \vec{P}_{sol}^2 /2M , \]  
(51)
corresponding to the kinetic soliton energy with recoil. For an atom in a box (50) transforms into
\[ E_{kin} = \frac{1}{2M} \left[ i \vec{\nabla}_a + : \int d\vec{r} \vec{\nabla}_a \Phi \Pi + : \right] 
+ : \int d\vec{r} \chi^+ i \vec{\nabla}_a \chi : \]  
(52)
Such a structure of the kinetic term could be easily verified from condition, that the transition into soliton (nuclei) rest frame should be a canonical transformation [35],[36]. But \( \vec{p}_a = -i \vec{\nabla}_a \) isn’t conserved yet. For the bosonic component \( \vec{\nabla}_a \) coincides up to the sign with \( \vec{\nabla}_r \), since the deformation of atomic nuclei by displacement is negligibly small, even if it approaches the cavity boundary, thence soliton mass in (52) remains the same as in (50). However, for the fermion field due to boundary condition (3) the dependence on \( \vec{a} \) and \( \vec{r} \) becomes by approaching the cavity boundary sufficiently diverse. Proceeding further, in nonrelativistic approximation for a one-particle fermion state, corresponding to the lowest atomic electron level, one finds from (52) the “recoil” effect in the form (49), since the lowest level electronic WF is real-valued and so \( \langle \psi_{el} | \vec{p}_a | \psi_{el} \rangle = 0 \), whereas \( \langle \psi_{el} | \vec{P}_{sol}^2 | \psi_{el} \rangle \neq 0 \). At the same time, the contribution of positron states (lower continuum of the Dirac equation) and the vacuum shift, which appear by taking average of operator (52) over one-electron valence state, are dropped, since they have sense only by taking account of relativistic corrections.

Now let us take into account, that in the spherical cavity \( E_0(a) \) and \( E_{rec}(a) \) are wittingly rotationally invariant, and so the initial \( SO(3) \) restores, the atomic state acquires rotational quantum numbers \( JM \), while the atomic energy levels in a cavity are defined from the radial equation
\[ \left[ -\frac{1}{2Ma^2}\partial_a(a^2\partial_a) + E_0(a) + \right. 
+ \left. \frac{J(J+1)}{2Ma^2} + E_{rec}(a) \right] \phi_{at} = E \phi_{at} . \]  
(53)
In (53) due to large nuclei mass the orbital term is important at the origin of coordinates only, while in \( E_{rec}(a) \) the matrix element \( \langle \psi_{el} | \vec{P}_{sol}^2 | \psi_{el} \rangle \) itself turns out to of the same order, as the electron kinetic energy and so \( E_0(a) \), and shows up the same growth for \( a \rightarrow R \). Moreover, in fact the angular part in \( \langle \psi_{el} | \vec{P}_{sol}^2 | \psi_{el} \rangle \) coincides precisely with corresponding term in \( \langle \psi_{el} | \vec{P}_{sol}^2 | \psi_{el} \rangle \). But due to the factor \( 1/2M \) the recoil term \( E_{rec}(a) \) turns out to be as small as the orbital one compared to \( E_0(a) \). As a result, in (53) the leading contribution to \( V_{eff} \) is given by the electronic energy \( E_0(a) \). In turn, due to kinetic energy of deformed electronic WF there appears a potential barrier in \( E_0(a) \) by \( a \rightarrow R \) (see Fig.10), which provides the confinement of atomic nuclei inside the cavity via its large mass.

Atomic ground state energy levels are given in Tab.4.
As expected, they are shifted from the minimum of the effective potential $E_0(\alpha)$ by several tenth of eV.

| $\lambda/\alpha$ | $E_{at}$ | $\Delta E_{at}$ |
|-----------------|---------|----------------|
| 0.8             | -14.174| 0.032          |
| 0.6             | -15.363| 0.11           |
| 0.3             | -18.663| 0.223          |
| 0.0             | -23.799| 0.345          |
| -0.3            | -30.906| 0.473          |
| -0.6            | -39.986| 0.604          |
| -1.2            | -64.509| 0.883          |

Tab.4. The lowest atomic level $E_{at}$ and its shift from the minimum of effective potential $\Delta E_{at} = E_{at} - V_{min}$ in eV for $R = 350$ and 7 values of $\lambda/\alpha$ from the range $-1.2 \leq \lambda/\alpha \leq 0.8$.

Radial components of ground state atomic WF and density distribution are shown on Fig. 11,12. Note, that within the initial problem statement there are no special boundary conditions imposed on the atomic nuclei. The confinement of nuclei inside the cavity volume proceeds dynamically by means of boundary condition (3) for the electronic WF, whence the deformation of the latter works for $a \to R$ as a spring, returning the nuclei back into the cavity volume. Moreover, if $\lambda = 0$, i.e. for Neumann boundary condition (5), which imply the possibility of periodic continuation of WF through the box boundary, an electron might be spread over a (sub)lattice compiled from cavities, filled in by atoms of the same type, as it proceeds in the Wigner-Seitz model [24]. But each nuclei should be confined in its own cell within a spherical shell localized inside the cavity, as it is shown on Fig.12.

6. Conclusion

So we have shown, that the properties of such a “not going out” atomic state might in some cases be sufficiently different from the confinement by a potential barrier. The most remarkable feature here is, that due to boundary condition (3) there come into play the nontrivial deformation properties of electronic WF under asymmetric distortion caused by interaction with the cavity boundary, whereas in the case of confinement by potential barrier the most essential role is played by WF “elasticity” under uniform pressure [11]-[16]. In particular, depending on the properties of the boundary the atomic position in the box center might turn out to be unstable and so the atom could be shifted towards the boundary. This displacement is accompanied with increase of the electronic bound energy and leads to spontaneous breakdown of initial $SO(3)$, thereon the Goldstone modes of atomic rotation restore the broken symmetry, the stationary atomic states acquire quantum numbers $JM_j$ of the total angular moment, while the atomic position becomes spread over a spherical shell in the vicinity of the box boundary (see Fig.12). The confinement of atomic nuclei proceeds dynamically due to the boundary condition (3) for the electronic WF — the deformation of the latter works for $a \to R$ as a spring, which returns the nuclei back into the box volume.

As a consequence, the properties of atomic H ground state turn out to be sufficiently different in dependence on the cavity parameters. For definite values of $R$ and $\lambda$ the energy of the lowest level could run due to displacement effect up to values, that exceed the bound energy of the atom in the center of cavity by dozens of eV, while in the limit of very large $R$ the regime of an atom, soaring over a plane with boundary condition (4), is reproduced, rather than a spherically symmetric configuration, what might be proposed on the basis of initial $SO(3)$ symmetry of the problem.

It should be noted also, that more complicated systems like molecular H ion behave in such a state with displacement towards the cavity boundary even more nontrivial, since due to boundary condition imposed on the elec-
tronic WF there changes itself the mechanism of molecular formation. To conclude let us emphasize once more, that the boundary condition (3) of “not going out” from the volume Ω doesn’t unavoidably imply an actual confinement of a particle inside Ω, as it occurs in the partial case of trapping by a potential barrier, but on the contrary, under definite conditions it allows for a much more wide problem statement, when a particle (electron) could be essentially delocalized [20]-[21]. In particular, within Wigner-Seitz model [24] such an approach leads to a consistent description of the lowest particle state in a cubic (sub)lattice, formed by microcages of the same type inside the parental crystalline matrix. In the latter case instead of single energy level there appears the whole set of states $\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k}\vec{r})$ with condition $u_{\vec{k}}(\vec{r}+\vec{b}) = u_{\vec{k}}(\vec{r})$, where $\vec{b}$ is the period of cavities sublattice, the wavevectors $\vec{k}$ fill in the first Brilluou zone, while the periodic WF corresponds to the state with $\vec{k} = 0$ and defines position of the zone bottom. A concrete example of such kind is given by the considered in sect. 4,5 case of atomic H for $\lambda = 0$, which describes situation, when all the cavities, occupied by atoms, form a (sub)lattice similar to that of an alkaline metal.

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