Quantum confinement under Neumann condition: atomic H filled in a lattice of cavities

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Energy spectrums of a nonrelativistic particle and an H-like atom in a spherical box of size $R$ with general conditions of “not going out” through the box surface are explored. The lowest energy levels reconstruction is described from the point of view of their asymptotical behavior for large $R$. The role of von Neumann-Wigner level reflection/avoided crossing effect in this spectrum reconstruction is emphasized. The properties of atomic H ground state in a cell, formed by a spherical cavity with an outer potential shell and Neumann condition on the outward boundary, are studied in detail. Some of them turn out to be quite new. The relevance of such a cell to a cubic lattice of cavities, occupied by H, is discussed be means of first principles and assumptions of the Wigner-Seitz model.

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1. Introduction

Considerable amount of theoretical and experimental activity has been focused recently on spatially confined atoms and molecules [1]-[6]. So far, starting from the works of Michels [7] and Sommerfeld [8], main attention has been devoted to the properties of atoms and molecules, confined by an impenetrable or partially penetrable potential barrier ([9], [10] and refs. therein). However, in reality general boundary conditions of “not going out” don’t unavoidably imply genuine trapping of a particle by a cavity, rather they could in some special cases correspond to a quite different picture, where the particle state undergoes delocalization from the box with definite symmetry properties of the wavefunction, as in the Wigner-Seitz model of alcaline metal [11]. 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 alcaline metal, like certain interstitial sites of a metal supercell, e.g. octahedral positions of palladium fcc lattice [12]-[14]. 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 the description of its ground state could be based on the first principles of the Wigner-Seitz model [11]. With the same assumptions as in [11], it turns out to be a special type of “confinement” under Neumann boundary condition in the corresponding Wigner-Seitz cell.

The purpose of this letter is to explore the features of such a type of “confinement” state in a cell, formed by a spherical cavity of radius $R$ with an outer potential shell of physically reasonable width and depth, and Neumann condition on the outward boundary. A number of nontrivial properties of such state, a part of which being similar to those described earlier for atoms trapped endohedrally inside a fullerene molecule [4], and more recently by means of general reflecting boundaries [15], while another part being quite new, is discovered by studying the asymptotical behavior of energy levels for large $R$. Moreover, such an approach allows for a valuable analysis of conditions, under which such phenomena could take place. In particular, we describe the case, when the ground state of atomic H considered as a function of $R$, contains a deep and strongly pronounced well, where the bound energy could be remarkably larger than that of 1s-level of the free atom $E_{1s}$, as well as the situation, when the lowest level reveals slowly decreasing power asymptotics for large $R$ and so its bound energy could exceed $E_{1s}$ for actual nanocavities with $R \sim 100 - 1000$ nm.

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

Stationary state of a particle with mass $m$ confined in a vacuum cavity $\Omega$ with boundary $\Sigma$ should be described by an energy functional of the following form

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

where $U(\vec{r})$ is the potential inside $\Omega$, while the surface term $\int_{\Sigma}$ corresponds to contact interaction of the particle with medium, in which the cavity has been formed, on the cavity boundary. The properties of this surface interaction are given by a real-valued function $\lambda(\vec{r})$.

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

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

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inside $\Omega$ combined with boundary condition imposed on $\psi$ on the surface $\Sigma$

$$\left[\vec{n}\vec{\nabla} + \lambda(\vec{r})\right]\psi|_\Sigma = 0 ,$$

(3)

with $\vec{n}$ being the outward normal to $\Sigma$.

Boundary condition (3) is known in mathematical physics as Robin’s (or third kind) condition, under which the spectral problem (2-3) is self-adjoint and so contains all the required properties for a correct quantum-mechanical description of a nonrelativistic particle confined in $\Omega$ [15],[16]. The particle “not going out” property is fulfilled here via vanishing normal to $\Sigma$ component of the quantum-mechanical flux

$$\vec{n}j|_\Sigma = 0 ,$$

(4)

where

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

(5)

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. In particular, such a picture takes place in the Thomas-Fermi model of many-electron atom [17], as well as in quark bag models of hadron physics [18],[19].

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

$$\vec{n}\vec{\nabla}\psi|_\Sigma = 0 ,$$

(6)

what corresponds to the boundary condition of confinement for a scalar field in relativistic bag models [18]. Moreover, condition (6) appears in the Wigner-Seitz model of an alcaline metal [11] and describes delocalization of valence electrons creating the metallic bond, by continuing the atomic wavefunction periodically in the lattice. Indeed such a “confinement” state is at the aim of our study.

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

$$\psi|_\Sigma = 0 ,$$

(7)

and so describes confinement by an impenetrable barrier.

There are two well-established and quite important inequalities for the ground state energy in the Dirichlet and Neumann cases of confinement [16]. The first one takes place for the Dirichlet problem (7) and tells, that if the volume $\Omega$ is embedded in volume $\Omega_1$, then $E(\Omega) > E(\Omega_1)$ for any nonsingular $U(\vec{r})$. Another one concerns the Neumann case (6) and gives the following estimate for the ground state energy

$$E_{ground}(\Omega) < \frac{\int_{\Omega} d\vec{r} U(\vec{r})}{\int_{\Omega} d\vec{r}} .$$

(8)

The inequality (8) follows immediately from the variational principle, if one considers a constant trial wavefunction in order to fulfill the boundary condition (6) in the simplest way. It can be easily generalized to the Robin’s case (3) in the following fashion. Let us consider the confinement state in $\Omega$ with no surface interaction, but with modified potential function

$$U_1(\vec{r}) = U(\vec{r}) + \frac{\hbar^2}{2m} \lambda(\vec{r}) \delta_{\Sigma_1}(\vec{r}) ,$$

(9)

where $\delta_{\Sigma_1}(\vec{r})$ denotes surface $\delta$-function with $\Sigma_1$ being a surface embedded in $\Omega$. The additional term in the modified potential $U_1$ gives rise to the following contribution to the energy functional

$$\Delta E[\psi] = \frac{\hbar^2}{2m} \int_{\Sigma_1} d\sigma \lambda(\vec{r}) |\psi|^2 ,$$

(10)

but at the same time doesn’t affect the Neumann boundary condition on $\Sigma$. The latter makes it possible to draw a direct analogy with the procedure leading to the inequality (8), since the trial wavefunction can be still chosen as a constant throughout $\Omega$. If we consider now the limit $\Sigma_1 \to \Sigma$ from the inside of $\Omega$, then the region $\Omega_1 \subset \Omega$ surrounded by the surface $\Sigma_1$ tends to $\Omega$, while the contribution of the region $\Omega - \Omega_1$ to energy becomes negligibly small. Proceeding further this way, we get the expression (1) as the limiting point for the energy functional, and so the following inequality for the ground state energy

$$E_{ground}(\Omega) < \frac{\int_{\Omega} d\vec{r} U(\vec{r})}{\int_{\Omega} d\vec{r}} + \frac{\hbar^2}{2m} \int_{\Sigma_1} d\sigma \lambda(\vec{r}) .$$

(11)

The estimates (8,11) turn out to be quite effective for understanding the ground state properties, especially for the case of extremely small cavities.

3. Robin’s reflecting boundaries

Now let us consider the case of Robin’s boundary condition (3). Since it has been already studied in [15],[16],[20],[21], we’ll point out here only those details, which are required for dealing with a more complicated and realistic model described in the next section.

First example is a particle in a spherical potential well of radius $R$ with a constant potential $U(\vec{r}) = U_0 , r < R$, and surface interaction $\lambda =$Const [15],[21]. In what follows, in order to provide an effective comparison of results, obtained for quite different systems, we’ll use relativistic units $\hbar = c = 1$, wavenumber and energy will be expressed in units of the particle mass $m$, while distances — in units of the particle Compton length $1/m$. Considering $U_0$ as a reference point for the particle energy, for s-levels one obtains

$$\tan kR = \frac{kR}{1 - \lambda R} .$$

(12)
where \( k = \sqrt{2E} \).

It is easy to see from (12), that the energy levels considered as functions of \( R \) reveal remarkably different behavior depending on the sign of \( \lambda \). More concretely, when \( \lambda > 0 \) and so describes reflection between the particle and environment, for \( R \to 0 \) the wavenumber of the lowest energy level behaves like \( \sqrt{3\lambda/R} \), while the ground state energy increases in the following way

\[
E_{\text{ground}}(R) \to \frac{3\lambda}{2R} , \quad R \to 0 ,
\]

what follows directly from eq. (12) as well as from the estimate (11). Such behavior of \( E_{\text{ground}}(R) \) confirms, that for confined systems the standard uncertainty relation should be replaced by a generalized one, which doesn’t imply, that for \( R \to 0 \) the kinetic energy of the particle could be estimated as \( O(1/R^2) \) (see [15],[22] and discussion therein). The latter should be definitely correct in the case \( \lambda \to \infty \) only, i.e. in the case of genuine trapping of the particle in a cavity by an impenetrable potential wall. For eq.(12) such behavior occurs for the particle states with positive energy in the case of surface attraction \( \lambda \leq 0 \), when for \( R \to 0 \) the wavenumber of the lowest energy level behaves like \( C/R \) with \( C = 4.49341 \) being the first root of the equation \( \tan x = x \), while the energy — like \( C^2/2R^2 \). For \( R \to \infty \) both types of solutions for the lowest positive level reveal the same asymptotics \( E(R) \to \pi^2/2R^2 \), what corresponds to the Dirichlet condition (7).

For \( \lambda < 0 \), i.e. for the case of attraction between the particle and environment, the generalized uncertainty relation for confined systems [15],[22] provides, that the ground state \( s \)-level lies below the well’s bottom and so should be found from eq.(12) via \( k \to ik \), i.e. from equation

\[
\tanh \kappa R = \frac{\kappa R}{1 + |\lambda|/R} .
\]

For \( R \to 0 \) the wavenumber \( \kappa(R) \) reveals the asymptotics \( \sqrt{3|\lambda|/R} \), hence

\[
E_{\text{ground}}(R) \to \frac{3|\lambda|}{2R} , \quad R \to 0 ,
\]

what could be easily verified by estimate (11) again. There are no contradictions with the general properties of the energy spectrum of a nonrelativistic particle here, since for \( \lambda < 0 \) the surface term in the expression (1) could be arbitrarily negative due to \(|\psi|^2\) on the box boundary, which might be now arbitrarily large without violating the normalization condition.

It should be noted also, that for \( R \to \infty \) such a level reveals the following asymptotics

\[
E_{\text{ground}}(R) \to -\lambda^2/2 - |\lambda|/R + O(1/R^2) , \quad R \to \infty ,
\]

and so its behavior on the whole half-axis \( 0 \leq R \leq \infty \) should be quite similar to a shifted downwards hyperbole.

Therefore for \( \lambda < 0 \) the particle lowest \( s \)-level lies below the well’s bottom even in the case of increasing well’s radius, but this property cannot be detected from estimate (11). The latter circumstance should be quite evident, since for large \( R \) the constant trial wavefunction cannot be a good approximation to the genuine wavefunction of the problem.

This example shows explicitly, that the spectrum of stationary states of a particle confined in a box with general “not going out” conditions could reveal features, which are quite different from the deconfinement case. In particular, for \( \lambda < 0 \) the behavior of the ground state is such, that the energetically most favorable state of a particle is to be caught by the smallest cavity.

The “not going out” state of atomic H with nuclei charge \( q \) in a spherical cavity with radius \( R \) and boundary conditions (3) turns out to be even more specific [15],[16],[20],[21]. As in the previous case, surface interaction is given by the constant \( \lambda \), while motionless point-like atomic nuclei is in the center of the cavity, then spherical symmetry is maintained and the ground state energy minimized. From the solution of the Schrödinger-Coulomb problem for the radial wavefunction of the electron state with orbital momentum \( l \) one obtains up to a numerical factor [17]

\[
R_l(r) = e^{-\gamma r} l^l \Phi(b_l, c_l, 2\gamma r) ,
\]

where

\[
\gamma = \sqrt{-2E} , \quad b_l = l + 1 - q/\gamma , \quad c_l = 2l + 2 ,
\]

and \( \Phi(b, c, z) \) is the confluent hypergeometric function of the first kind (Kummer function). Definition, notations and main properties of the Kummer function follow ref. [23]. Substituting (17) 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

\[
\Phi_R = \Phi(b_l, c_l, 2\gamma R) , \quad \Phi_R(b+) = \Phi(b_l + 1, c_l, 2\gamma R) .
\]

As in the previous case of a potential well, the most significant changes in the spectrum take place for \( R \to 0 \), what could be seen at once from the estimate (11). Here it should be noted, that for atomic H the limit \( R \to 0 \) takes 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 [21]. 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 \( R \sim 10 \). To underline the existence of this lower limit, the curves shown on Figs. 2-6 below will start from \( R = 10 \) too.

There are two types of the lowest level of 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
\[
\gamma(R) = \gamma_0 + \gamma_1 R + \gamma_2 R^2 + \ldots .
\] (21)
Expanding $\Phi_R, \Phi_R(b+)$ in a power series in $R$ (what is always possible, since the Kummer series converges everywhere in the complex plane), to the lowest order one obtains from (19) that $l = 0$, and by proceeding further
\[
\lambda = q , \quad \gamma_0^2 = q^2 , \quad \gamma_n = 0, \quad n \geq 1 .
\] (22)
It follows from (22), that if $\lambda = q$, then the ground state energy of atomic H in a cavity for any $0 \leq R \leq \infty$ precisely coincides with that of $1s$-level of the free atom
\[
E_{\text{ground}}(R) = E_{1s} = -q^2/2 ,
\] (23)
what has been already mentioned in [16],[20].

More precisely, for $l = 0$, $\lambda = q, \gamma_0 = \pm q$ eq. (19) is satisfied for all $R$. For $\gamma_0 = q$ it is provided by $b_0 = 0$ and $\Phi(0, 2, z) = 1$, while for $\gamma_0 = -q$ one obtains $b_0 = 2$, $\Phi(2, 2, z) = e^z$, $\Phi(3, 2, z) = (z/2 + 1)e^z$, and in both cases substitution into (19) gives an identity. There is however no twofold degeneracy of the level, since both signs in $\gamma_0 = \pm q$ correspond to the same radial $1s$-function $R_0(r) = Ae^{\sqrt{q}r}$, what should be quite obvious, because the parameter $\gamma$ is defined via relation $E = -\gamma^2/2$, where the sign of $\gamma$ isn’t fixed.

As for a particle in a potential well, another type of levels reveals for $R \to 0$ asymptotic behavior similar to (13) or (15) and is found by assumption, that in the vicinity of $R = 0$ the wavenumber $\gamma$ is represented by a series
\[
\gamma(R) = \frac{\xi}{\sqrt{R}} + \xi_0 + \xi_1 \sqrt{R} + \ldots .
\] (24)
Substituting (24) into eq. (19), to the lowest order in $\sqrt{R}$ one obtains again $l = 0$, while higher orders of expansion in $\sqrt{R}$ yield
\[
\xi^2 = 3(q - \lambda) , \quad \xi_0 = 0 , \quad \xi_1 = \frac{q^2 + 3q\lambda + 6\lambda^2}{20\xi} , \quad \ldots .
\] (25)
As a result, for such type of $s$-levels of H in a cavity one obtains the following dependence on the cavity radius for $R \to 0$
\[
E_{\text{ground}}(R) \to -\frac{3(q - \lambda)}{2R} - \frac{q^2 + 3q\lambda + 6\lambda^2}{20} + O(\sqrt{R}) ,
\]
\[
R \to 0 .
\] (26)
Qualitative explanation of linear dependence on $q$ and $\lambda$ is quite simple. As for a particle in a spherical well, for $R \to 0$ the atomic wavefunction of such $1s$-level inside a cavity becomes almost constant, and so the estimate (11), which reproduces the first term in (26), turns out to be almost exact too. The numerical solution of eq.(19) for $q = \alpha \simeq 1/137$ and $\lambda = (1 \pm 0.01)q$, $\lambda = (1 \pm 0.02)q$ shows, that the behavior of such $s$-levels tends to the asymptotics (26) for $R$ of order about several tenths of $a_B = 1/\alpha \simeq 137$ (Fig.1).

The analogy between a particle in a well and H in a cavity remains valid for $R \to \infty$ too, where it could be easily checked by means of asymptotic expansion for $\Phi_R$, $\Phi_R(b+)$ in (19), that in the case of surface attraction $\lambda < 0$ there exists one more level $\tilde{E}(R)$ with negative limiting value $\tilde{E}(\infty) = -\lambda^2/2$, besides the discrete spectrum of the free atom, and power asymptotical behavior for $R \to \infty$
\[
\tilde{E}(R) \to -\lambda^2/2 - (q + \lambda)/R + O(1/R^2) , \quad R \to \infty .
\] (27)
For $\lambda < -q < 0$ this analogy could be extended on the whole range of cavity sizes, since under these conditions $\tilde{E}(R)$ turns out to be the lowest atomic $s$-level with the form of shifted downwards hyperbole, as for a particle in a well.

Now let us turn to the next type of atomic levels in a cavity, which appear under assumption, that $\gamma R$ remains finite for $R \to 0$. To maintain the connection with two previous types of levels, we consider only $s$-levels with $l = 0$ and rewrite (19) in the form
\[
(2\partial/\partial z + \lambda/\gamma - 1)\Phi(1, 2, z)|_{z=2\gamma R} = 0 .
\] (28)
Since $\gamma \to \text{Const}/R$ for $R \to 0$, then $\lambda/\gamma \to 0$, $b_0 = 1 - q/\gamma \to 1$, and so (28) transforms into
\[
(2\partial/\partial z - 1)\Phi(1, 2, z)|_{z=2\gamma R} = 0 .
\] (29)
Taking account of $\Phi(1, 2, z) = (e^z - 1)/z$, from (29) one obtains
\[
\gamma R = ix_n , \quad \tan x_n = x_n ,
\] (30)
what describes positive energy levels with the asymptotics
\[
E_n(R) \to \frac{x_n^2}{2R^2} , \quad R \to 0 ,
\] (31)
i.e. excited states of a particle (electron) in a well with Neumann boundary conditions (6). So all the s-levels besides 1s (provided that the latter turns out to be the lowest one and falls down for $R \to 0$, what implies $|\lambda| < q$) should for $R \to 0$ reveal asymptotical behavior (31), while levels with $l \neq 0$ lie even higher due to the centrifugal term. At the same time, for $R \gg 1$ all the ns-levels (as well as levels with $l \neq 0$) tend to their asymptotical values, corresponding to those of the free atom, exponentially fast

$$E_n(R) - E_n \to \frac{\gamma_n}{n!}^2 \frac{\lambda - \gamma_n}{\lambda + \gamma_n} (2\gamma_n R)^{2n} e^{-2\gamma_n R},$$

$$\gamma_n R \gg 1,$$  \hspace{1cm} (32)

where

$$E_n = -\gamma_n^2/2, \quad \gamma_n = q/n, \quad n = 1, 2, \ldots,$$  \hspace{1cm} (33)

are the 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 (32) turns out to be an exceptional feature of those confined atom 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 atomic levels in a cavity, which originate from the continuous spectrum of the free atom and the additional level (27), 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 $\tilde{E}(\infty) = -\lambda^2/2$.

If $\lambda = \pm \gamma_n$, the asymptotics (32) 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

$$E_n(R) - E_n \to (n - 1) \frac{\gamma_n}{n!}^2 (2\gamma_n R)^{2(n-1)} e^{-2\gamma_n R},$$

$$\gamma_n R \gg 1,$$  \hspace{1cm} (34)

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 (32) one obtains

$$E_n(R) - E_n \to \frac{1}{n + 1} \frac{\gamma_n}{n!}^2 (2\gamma_n R)^{2(n+1)} e^{-2\gamma_n R},$$

$$\gamma_n R \gg 1,$$  \hspace{1cm} (35)

and moreover, the limiting point $\tilde{E}(\infty)$ of the level $\tilde{E}(R)$ with the power asymptotics (27) coincides with the corresponding level $E_n$ of the free atom (33), what in turn represents a remarkable example of von Neumann-Wigner avoiding crossing effect, i.e. near levels reflection under perturbation [17], [24] — 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 wavefunction doesn’t vanish on the cavity boundary, and so for $R \gg 1$ 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 (35), while $\tilde{E}(R)$ goes downwards according to the asymptotics

$$\tilde{E}(R) \to E_n - \frac{n + 1}{n} \frac{q}{R} + O(1/R^2), \quad R \to \infty.$$  \hspace{1cm} (36)

So the energy spectrum of atomic H (with $q > 0$), confined in a cavity with Robin’s condition (3), turns out to be the following. For $\lambda = q$ the lowest s-level acquires the constant value $E_{1s}$ of the free atom, for $\lambda > -q$ it behaves for $R \to 0$ according to (26) with an energy shift depending on sign $(\lambda - q)$ and for $R \gg 1$ it approaches $E_{1s}$ exponentially fast, while for $\lambda \leq -q < 0$ it transforms into the level $\tilde{E}(R)$ with power asymptotics (27). Excited states in all the cases should for $R \to 0$ reveal the behavior (31). And for an H-like atom there once more takes place the situation, similar to that for a particle in a potential well, namely — whenever $\lambda < q$, the atomic state with largest bound energy, which could sufficiently exceed the bound energy of the lowest level of the free atom (23), takes place in the smallest cavity.

4. Atomic H in the Wigner-Seitz cell

So far, by formulating the confinement problem (2-3) it was implied, that a particle in such a “not going out” state interacts with environment only on the cavity boundary $\Sigma$, i.e. through certain $\delta$-like potential, what leads to the surface term in the energy functional (1). In a more realistic approach one should consider instead of a $\delta$-like interaction an outer potential shell of nonvanishing thickness $d$, into which the particle penetrates and interacts there with cavity environment. In the limit $d \to 0$ such potential shell should transform into contact interaction on the surface $\Sigma$. For these purposes the boundary condition (3) should be replaced by an equation of Schroedinger type, describing particle interaction with medium inside the shell, whose potential might be quite different from $U(\vec{r})$. In the case of spherical cavity and shell the first choice for the shell potential is a constant $U_0$, as by modelling the endohedral environment
where $\kappa^2 = 2(U_0 - E)$, while all the other quantities are defined as in (18) and (20). It is easy to see, that the relation (39) gives
\[ \kappa R \frac{1 - \kappa X \tanh \kappa d}{\tanh \kappa d - \kappa X} \to \lambda R - 1, \quad d \to 0, \quad (41) \]
whence it follows, that for $d \to 0$ eq.(40) transforms into eq.(19) for atomic $s$-levels with boundary condition (3).

It should be specially remarked, that the limits $d \to 0$ and $R \to 0$ don’t commute either. In particular, if $d \neq 0$, then for the lowest $s$-level the solution of eq.(40) for $R \to 0$ leads to
\[ E_{\text{ground}}(R) \to U_0, \quad R \to 0. \quad (42) \]
The latter could be easily detected from (11), which in this case gives
\[ E_{\text{ground}}(R) < E_{\text{trial}}(R) = \]
\[ = \frac{3R^2 + 3Rd + d^2}{(R + d)^3} U_0 d - \frac{3R^2}{2(R + d)^3} q, \quad (43) \]
and $E_{\text{trial}}(R \to 0) \to U_0$, combined with the above-mentioned feature, that for $R \to 0$ the estimate (11) turns out to be exact.

More precisely, there are two types of solutions of eq.(40) for $R \to 0$. The first one originates from (40) by neglecting the term with $\kappa R$ and omitting the common factor $(\tanh \kappa d - \kappa X)$, what leads to the following relation
\[ (q/\gamma - \gamma R)\Phi_R + (1 - q/\gamma)\Phi_R(b+) = 0. \quad (44) \]
For $R \to 0$ eq.(44) contains no solutions with finite energy, since when $\gamma R \to 0$, then $\Phi_R$, $\Phi_R(b+) \to 1$, hence (44) reduces to $1 = 0$, and otherwise, when $\gamma R \to \text{Const} \neq 0$, then $q/\gamma \to 0$ and $b_0 \to 1$, hence (44) could be simplified up to
\[ z\Phi(1, 2, z) = 2\Phi(2, 2, z). \quad (45) \]

Eq.(45) in turn reduces to $e^z + 1 = 0$, whence $\gamma_n = i(\pi/2 + \pi n)/R$, which corresponds to a series of highly excited $s$-states with energies
\[ E_n \to \frac{(\pi/2 + \pi n)^2}{2R^2}, \quad R \to 0. \quad (46) \]
The second type of solutions of (40) for $R \to 0$ emerges from the factor $(\tanh \kappa d - \kappa X)$, what gives $\kappa_n = ix_n/d$ with $x_n$ being the solutions of eq. (44) which leads to another series of $s$-levels, corresponding to the energy spectrum of a particle in a well of radius $d$ and Neumann boundary condition (6,38)
\[ E_n = U_0 + \frac{x_n^2}{2d^2}. \quad (47) \]
These levels reveal a finite limit for $R \to 0$, while the lowest one, corresponding to $x_0 = 0$, meets the limiting value $E_0(R \to 0) = U_0$.

It is easy to verify, that there are no solutions of eq. (40) for $R \to 0$ besides (46) and (47). So the effect of infinite descent of the lowest level for $R \to 0$, which takes place in the case of contact surface interaction for $\lambda < q$, doesn’t occur for the potential shell of nonvanishing width.

The physical meaning of series (46, 47) should be quite clear. The levels (46) correspond to $s$-states of continuous spectrum of the free atom, when the latter is confined in a cavity with $R \to 0$, while the levels (47) originate from $ns$-levels with exponential asymptotics (32) and a finite number of levels $\tilde{E}_k$ with power asymptotics for $R \to \infty$, which appear for $U_0 < 0$ and turn out to be direct analogies of $E(R)$ for the case of contact interaction with $\lambda < 0$ (27).

Compared to the case of contact interaction (32), the asymptotics of $ns$-levels for $R \gg 1$ is modified in the following way

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

$$\gamma_n R \gg 1,$$  

(48)

where

$$\kappa_n = \sqrt{2U_0 + \gamma_n^2},$$  

(49)

while $E_n$ and $\gamma_n$ are defined as in (33). It follows from (48), that for

$$|\kappa_n \tanh(\kappa_n d)| < \gamma_n$$  

(50)

the curves $E_n(R)$ approach the $ns$-levels of the free atom (33) for $R \gg 1$ from below, while for $|\kappa_n \tanh(\kappa_n d)| > \gamma_n$ from above. Therefore the curves $E_n(R)$ could for finite $R$ reveal nontrivial minima, which lie below the corresponding $ns$-levels of the free atom (33), provided that the relation (50) is satisfied. The specific feature of the problem with an outer shell is that now such a minimum, and the deepest one, exists for the lowest $s$-level as well, whereas for vanishing width of the shell and $\lambda < q$ this level should for $R \to 0$ reveal an infinite falldown, and so nontrivial minima could appear for excited states only. A crude estimate for such a minimum for the lowest $s$-state can be received from inequality (42) by solving $\partial E_{\text{trial}}(R)/\partial R|_{R_0} = 0$, what gives

$$R_0 = \frac{2qd}{q - 2U_0d},$$  

(51)

and

$$E_{\text{trial}}(R_0) = \frac{1}{d} \left[4(U_0d)^3 - 16q(U_0d)^2 + 19q^2U_0d - 6q^3\right] \times$$

$$\times [4(U_0d)^3 - 16q(U_0d)^2 + 19q^2U_0d - 6q^3].$$  

(52)

The eq. (51) predicts the existence of a nontrivial minimum for the lowest state only when $2U_0d < q$, what is more crude, than the exact relation (50). The difference, however, should be quite clear, since the estimate (11) works well only for small cavities of such type, hence for small $d$, when $2U_0d$ should be identified with $\lambda$ and so $2U_0d < q$ is nothing else, but the relation $\lambda < q$.

As for the boundary condition (3), the asymptotics $\tilde{E}_k(\infty) = \tilde{E}_k$ of power levels $\tilde{E}_k(R)$ with negative limiting values for $R \to \infty$ is found from (40) by taking account of the main exponential term in the asymptotics of the Kummer function, what yields the following relation

$$\tilde{k}_k \tanh(\tilde{k}_k d) + \tilde{\gamma}_k = 0,$$  

(53)

where $\tilde{k}_k = \sqrt{2U_0 + \tilde{\gamma}_k^2}$, $\tilde{E}_k = -\tilde{\gamma}_k^2/2$. Note, that if $\tilde{\gamma}_k = \gamma_n$, i.e. the levels $\tilde{E}_k$ and $E_n$ possess the same limiting value for $R \to \infty$, then the l.h.s. of (53) coincides with the denominator in the asymptotics of exponential levels (48). So vanishing denominator in (48) implies once more the change in the asymptotical behavior of the exponential level due to the Neumann-Wigner reflection effect, what is discussed in detail for the case of the lowest level below.

It follows from (53), that such power levels with $\tilde{E}_k < 0$ might appear only for $U_0 < 0$, when (53) takes the form

$$\sqrt{2|U_0| - \tilde{\gamma}_k^2} \tan\left(\sqrt{2|U_0| - \tilde{\gamma}_k^2} d\right) = \tilde{\gamma}_k,$$  

(54)

and is nothing else but the equation for even levels in one-dimensional square well of width $2d$ and depth $U_0$. Therefore the levels $\tilde{E}_k$ exist for any $U_0 < 0$ and $d > 0$, their values lie in the interval $U_0 < \tilde{E}_k < 0$, while their total number $K$ is defined from $\pi(K - 1) < 2|U_0|d < \pi K$, $K = 1, 2, \ldots$.

The asymptotics of the levels $\tilde{E}_k(R)$ for $R \to \infty$ takes the form

$$\tilde{E}_k(R) \to \tilde{E}_k - \frac{q}{R} \frac{|U_0| + \tilde{E}_k}{|U_0| (1 + \tilde{k}_k d)} \frac{1}{1 + \tilde{\gamma}_k d} O(1/R^2),$$

$$R \to \infty.$$  

(55)

Note, that in such a problem there exist other power levels with $\tilde{E}_k > 0$, which correspond to imaginary wavenumbers $\tilde{\gamma}_k$ and so should be found from the asymptotics of the Kummer function including the power term besides the exponential one, but these levels lie wittingly higher, than the power (55) and exponential (48) ones, whereas our main interest is first of all bent on the lowest atomic levels.

Another crucial difference between power $\tilde{E}_k(R)$ and exponential $E_n(R)$ levels is that the origin of the formers is the attractive interaction between the particle (atomic electron) with cavity boundary (outer shell), rather than the interaction with the inner shell (atomic nuclei). In
takes place at infinitely increasing contrary, the H state with the lowest energy is achieved lowest energy atomic H state coincides with the exponential shell, in the limit $R \to \infty$. In a slightly different language, this circumstance has been pointed out in [4, 15].

A more detailed analysis of eq.(40) turns out to be most conveniently performed by means of its numerical solution for a concrete set of parameters $U_0$ and $d$, corresponding to realistic scales of microcavities, in which such a “confined” H state could occur (to simplify the discussion, henceforth we’ll deal with energy in eV). For $|U_0|$ this is $1 - 100$ eV, for $d$ — fractions of the Bohr radius $a_B = 1/\alpha \simeq 137$, more concretely $d = xa_B$ with $x = 2^{-p}$, $p = -1, 0, 1, ..., 4$, where the largest $2a_B$ is chosen according to the mean width of one-atom surface shell, while the smallest $a_B/16$ — in accordance with the lower limit, following from relativistic effects [21]. The range of values for $|U_0|$ is defined by taking into account, that $|U_0|$ could vary from $\sim 1$ eV for vacuum “bubbles” in superfluid He^4 [6] up to dozens eV in quantum chemistry [1]-[5].

The most simple and transparent example is given by the potential barrier $U_0 > 0$. In this case the lowest energy atomic H state coincides with the exponential 1s-level, whose behavior as a function of $R$ for $U_0 = 10$ eV is shown on Fig.2 (for $R \geq 10$). In accordance with relation (50), which in this case gives $d < 100$, there are pronounced minima for such $U_0$ and $d = a_B/4, a_B/8, a_B/16$ on the curves $E_1(R)$, and so a cell with such parameters turns out to be an effective H-trap. A minimum exists also for $d = a_B/2$, but here it is quite weak (bound energy exceeds only $\sim 13, 9$ eV) and takes place at $R = 289$, while for $d = a_B, 2a_B$, on the contrary, the H state with the lowest energy is achieved for infinitely increasing $R$.

The behavior of the lowest level reveals a more pronounced dependence on $d$, as well as on $U_0$, in the case of attraction in the outer shell ($U_0 < 0$) due to increased amplitude of electronic wavefunction near the outward boundary. In particular, for $U_0 = -10$ eV (Fig.3) the relation (50) is fulfilled for all $d$, hence nontrivial minima in the bound energy exist now for all $d$, including $d = 2a_B$, when a minimum with bound energy $14, 8$ eV is achieved at $R = 254$.

Now let us consider the most interesting case of energy levels reconstruction for atomic H in a cavity with such an attraction in the outer shell, that the lowest atomic level turns out to be the power one $E_1(R)$. For these purposes the “critical” potential $U_{0 \text{ crit}}$, which provides the coincidence of $E_1(\infty)$ with the limiting value of the first exponential level $E_1(\infty) = E_{1s}$, what implies

$$\gamma_1 = \gamma_1, \tag{57}$$

should be firstly determined.

The form of $U_{0 \text{ crit}}$ as a function of the shell width $d$ is shown on Fig.4. Above $U_{0 \text{ crit}}(d)$ there lies the region of $U_0$ and $d$, where the lowest level turns out to be the exponential $E_1(R)$, while below — the region, where the power $E_1(R)$ is the lowest.
It is easy to find from eqs.\,(53, 57), that for $d \to \infty$ the limiting value of $U_{0 \text{ crit}}(d)$ should coincide with the lowest level of the free H \,(23) with the following asymptotics

$$U_{0 \text{ crit}}(d) \to E_1 s - \frac{\pi^2}{8d^2} + \frac{\pi^2}{4qd^4} + O(1/d^4), \quad d \to \infty,$$

(58)
while for $d \to 0$ the “critical” potential decreases according to

$$U_{0 \text{ crit}}(d) \to -q/2d, \quad d \to 0.$$  \hspace{1cm} (59)

The numerical values of $U_{0 \text{ crit}}$ for $d$ under consideration are presented in Tab.\,1 (besides $d = a_B/16$, since in this case $|U_{0 \text{ crit}}|$ turns out to be too large).

| $x = d/a_B$ | 1/8  | 1/4  | 1/2  | 1    | 2    | 4    | 16   |
|-------------|------|------|------|------|------|------|------|
| $U_{0 \text{ crit}}$, eV | $-118.9$ | $-64.2$ | $-37.0$ | $-23.7$ | $-17.6$ | $-15.0$ | $-13.7$ |

TAB.\,1: The values of $U_{0 \text{ crit}}$ for $d = xa_B$.

The behavior of the curves $E_1(R)$ and $\tilde{E}_1(R)$ for $U_0 = 0.9 \; U_{0 \text{ crit}}$ and $U_0 = U_{0 \text{ crit}}$ is shown on Fig.\,5 for $d = a_B$. It is easy to recognize here the effect of avoided crossing, discussed in \,[4, 15], which shows up now in the change of asymptotics of the lowest level, when the value of $U_0$ coincides with $U_{0 \text{ crit}}$.

It should be emphasized, that the change of the lowest level asymptotics for $R \to \infty$ from exponential into the power one takes place indeed when $U_0$ reaches $U_{0 \text{ crit}}$ from above, not earlier and not later. In this case the limiting point $E_{1s}$ of the free atom is the same for the curves $E_1(R)$ and $\tilde{E}_1(R)$, and so as for the case of contact interaction \,(35,36), the exponential level $E_1(R)$ should approach its limiting point from above, thence the power $E_1(R)$ turns out to be the lowest one due to the Neumann-Wigner reflection. Let us underline specially, that it is indeed an exchange of asymptotical behaviour for the lowest level — the levels $E_1(R)$ and $\tilde{E}_1(R)$ could be infinitely close to each other, but don’t touch and all the more that intersect, since all the s-levels in such a problem cannot be degenerate. Note also, that this exchange of asymptotical behavior proceeds in the following way — when $U_0 \to U_{0 \text{ crit}}$ from above, the denominator in the r.h.s. of \,(48) tends to zero, hence the exponential tail of the curve $E_1(R)$ is shifted to more and more large $R$, for $U_0 = U_{0 \text{ crit}}$ it disappears completely, and so the power behavior extends to the whole half-axis $0 < R < \infty$.

The behavior of the level $\tilde{E}_1(R)$ for $U_0 = U_{0 \text{ crit}}(d)$, i.e. at the moment when it becomes the lowest one, is shown on Fig.\,6 for $d = 2^p a_B$ with $p = -1, 0, \ldots, 3$. (The case $d = a_B/16$ is omitted, since $U_0$ and the upper limit of bound energy acquire in this case too large values $U_0 \sim -240 \text{ eV}$, bound energy $> 300 \text{ eV}$, and so in background of the curve for $d = a_B/16$ the details of the other curves become illegible.)

Fig.\,6 shows explicitly the power asymptotics of the level $\tilde{E}_1(R)$ for $R \to \infty$. The shift of power levels relative to their asymptotical value decreases sufficiently slower than that of the exponential ones, which arrive at their asymptotics for $R$ of order of several $a_B$ already, and so such a “confined” atomic H state turns out to be energetically favorable up to actual nanoscales, provided that $U_0 \leq U_{0 \text{ crit}}(d)$. Numerical values (in eV) for the shift of bound energy of the power level $\tilde{E}_1(R)$
relative to the free H are given in Tab.2 for a cavity of nanosize with \(U_0 = U_{0\text{crit}}(d)\), i.e. at the moment when \(\tilde{E}_1(R)\) transmutes into the atomic H ground state, for \(d = a_B, a_B/2, a_B/4\).

| \(R\) | 1 nm | 10 nm | 100 nm | 1000 nm |
|-------|------|-------|--------|---------|
| \(\Delta E(d = a_B)\) | 1.00894 | 0.102517 | 0.0102667 | 0.00102686 |
| \(\Delta E(d = a_B/2)\) | 1.5722 | 0.157199 | 0.0157202 | 0.00157203 |
| \(\Delta E(d = a_B/4)\) | 2.08505 | 0.20661 | 0.0206425 | 0.00206407 |

TAB. 2: The values of \(\Delta E = E_{1s} - \tilde{E}_1(R)\) in a nanocavity with \(U_0 = U_{0\text{crit}}(d)\), when \(\tilde{E}_1(R)\) transmutes into the lowest atomic level.

5. Conclusion

To conclude let us firstly mention, that a single cavity might be just a simple hollow cage without any special confining property, but a large set of cavities, forming a cubic lattice, could reveal such properties due to quantum coherence effects, similar to those creating the metallic conﬁning property, but a large set of cavities, forming a crystal structure similar to that of an alcaline metal. In particular, in dependence on the outer shell parameters the upper limit for the bound energy of H in such a cell could be more large, than several times the bound energy of the lowest 1s-level of the free atom. At the same time, in the case of a power lowest level the bound energy decreases very slowly for increasing cavity size, therefore such a state should be energetically favorable compared to the free atom up to actual nanocavities with \(R \sim 100 - 1000\) nm. The latter circumstance means, that artificial macroscopic lattices, created from such nanocavities in suitable media, could serve as quite effective containers of H. Even more interesting results for searching possible new effects appear in the case of more complicated atoms and simplest diatomic molecules in such a cell and a lattice with the same parameters as employed in sect.4 [25].

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