

Chapter 2

Symmetry Reduction and Energy Levels

Splitting of the One-Electron Atom in an Impenetrable Cavity

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2.1 Introduction

The splitting of a degenerate energy level is one of the oldest quantum-chemical problems. Here we consider this problem for some simple one-electron systems placed in an impenetrable cavity. The Hamiltonian of the model systems considered here has the form

$$H = -\frac{1}{2}\Delta + V(|\mathbf{r}|) \quad (2.1)$$

where \mathbf{r} is electron radius-vector and V is the spherically symmetric potential; here and later we use only atomic units. Problems of this type appeared first in the Solid State Theory, where one of the first models was closely connected with the solution of the one-electron Schrödinger equation in a bounded region Ω with Neumann boundary conditions on the wavefunctions $\varphi(\mathbf{r})$ [1, 2]: the derivative along the external normal \mathbf{n} to the boundary $\partial\Omega$ of the region vanishes. That is,

$$\partial_n \varphi(\mathbf{r})|_{\mathbf{r} \in \partial\Omega} = 0 \quad (2.2)$$

Here the normal derivative is denoted as $\partial_n = (\mathbf{n}, \nabla_{\mathbf{r}})$; $\nabla_{\mathbf{r}}$ is the gradient symbol with respect to the particle coordinates.

It is natural, that one of the first problems studied was the problem of the particle in a spherical cavity and corresponding energy changes under the sphere extension [3–5]. For this problem some other types of the boundary conditions also were studied; for example, the Dirichlet conditions that define the impenetrable cavity

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$$\varphi(\mathbf{r})|_{\mathbf{r} \in \partial\Omega} = 0 \quad (2.3)$$

The general self-adjoint boundary conditions were also studied in [6] for some parameter κ :

$$\partial_n \varphi(\mathbf{r}) - \kappa \varphi(\mathbf{r})|_{\mathbf{r} \in \partial\Omega} = 0 \quad (2.4)$$

For a review of mathematical problems for boundary conditions (2.1–2.4), in particular for the case when κ depends on some parameters, see in [7, 8]. We restrict this study to Dirichlet boundary conditions (2.3).

The work of Michels et al. [9] is often regarded as a first example of how the Dirichlet boundary conditions can be applied to study real physical problems. In this work, the hydrogen atom under high pressure was studied. Note that the approach is still in use, especially in astrophysics [10]. Another domain of applicability is connected with modeling of defects in solids, superlattice structures, quantum dots and quantum wires.

For example, excitons in semiconductors may be described as an electron-hole pair. The differences with the hydrogen-like systems are here mainly in the effective masses of particles and the polarization of the medium around the cavity. A large number of examples and applications for the model of the atom embedded in a cavity may be found in [11–13]. In [14] the interaction of embedded particles with the cavity walls is considered. See also the other papers from the issue cited.

The problem of a spherically symmetric system placed at the centre of impenetrable spherical cavity allows for reduction to independent 1D problems; see e.g. [15, 16]. The hydrogen atom problem in impenetrable spherical cavity is described in details in [17]. The works [7, 16, 18, 19] summarize the energy spectrum description for boundary conditions of general type (2.4). The 2D and 3D harmonic oscillator in a spherical cavity problem is described in details in [20, 21].

The model of an atom in a cavity is often used to simulate the states of atoms embedded in fullerenes or carbon nanotubes [22]. Note that the question of how free is the atom or the molecule inside the cavity of a nanotube or a fullerene is raised from time to time [23–26].

Closely related to the confined atom problems are the problems of the Crystal Field theory and this is well known (see e.g. [27–31]). Effect of restrictions of the region of free movement of electrons on the matrix elements of the perturbation operator associated with the system of point charges was discussed, for example, in the context of the crystal field theory in [31, 32].

The most common effect of symmetry reduction of the spherically symmetric system under the influence of applied external field consists of splitting of degenerate energy levels. In this paper, we consider similar effects for one-electron systems in a cavity when Dirichlet boundary conditions are imposed. Such problems require the study of cavities of more general form than purely spherical ones.

Below we use the symbols $\varphi_j(\mathbf{r}, \Omega)$, $E_j(\Omega)$ (or φ_j when the region is fixed and clear) for eigenfunctions of the Hamiltonian (2.1) under the Dirichlet boundary

conditions (2.3). For the free atom problem (i.e. for $\Omega = \mathbb{R}^3$ and the condition that the wavefunctions are square-integrable) the eigenfunctions of H and corresponding energies of the discrete spectrum are denoted as ψ_j , E_j . The energy levels are enumerated in increasing order. All the functions used here are real-valued.

2.2 Effects of Symmetry Lowering for Cavities of Different Type

2.2.1 Spherical Cavity

The symmetry reduction in passing from the free system to the system in a cavity is a well-known phenomenon. For example, the particle moving in the pure Coulomb field possesses a higher dynamic symmetry than a general spherical one. This is the reason for the high degeneracy of the energy levels. The energy is the same for the states (n, ℓ) with the same principal quantum number n and different angular momentum values [33]. However, for the hydrogen atom with the nucleus placed in the center of impenetrable spherical cavity of finite radius R , the degeneracy mentioned disappears. See the analysis of the energy levels for this problem in [17].

There exist a number of explanations for this phenomenon, but here we mention only one of them. The extra degeneracy of the free hydrogen atom energy levels is the result of the so called Lenz vector conservation [33] being a specific integral of the motion for the Kepler problem in classical mechanics; this conservation law implies constant orientation and shape of the elliptical orbit. When the atom is placed in a spherical cavity, then the classical electron moves along the elliptical orbit, but is then reflected from the spherical surface. The orbit is formed by the system of elliptical fragments and the Lenz vector does not conserve. (The quantum mechanical description of the problem in terms of Dirichlet boundary conditions violations may be found in [34]). Nevertheless one may find that when the cavity radius R equals the square of the angular momentum for any energy value, all the orbits are closed and consist of exactly two elliptical fragments. This is the case when the system “remembers” the additional conservation law [35] of its free state. This is followed by a surprising degeneracy of quantum states $(n, \ell + 2)$ and $(n - 1, \ell)$, being simultaneous for any $n > \ell + 2$ when $R = (\ell + 1)(\ell + 2)$ [17, 34]. For example, for $R = 2$ au one may find relations $E_{2s}(R) = E_{3d}(R)$, $E_{3s}(R) = E_{4d}(R)$, For the specific R noted the lowest energy of the state with momentum ℓ of the hydrogen atom equals exactly to the energy of the free atom in the state $(\ell + 2, \ell)$.

These regularities are closely connected with the properties of confluent hypergeometric function that defines the radial wavefunctions of hydrogen-like atom [17]. It is not strange that simultaneous degeneracy can be found in some other problems, for example, for the confined isotropic harmonic oscillator in an impenetrable spherical cavity [36]. For the description of the details in similar situations, see also [20, 21, 37].

In a more general case of the spherically symmetric potential one may find only the usual $2\ell + 1$ -fold degeneracy of the states with different angular momentum projections, that is, due to the conventional spherical symmetry of the problem. One may note only, that the energy of the state (n, ℓ) increases both with n and ℓ . Extension of any cavity is accomplished with monotonic decreasing of each of the energy levels (see [38], Sect. XIII.15, or [39]) that converge to the corresponding $E_{n\ell}$ levels of the free system. A general statement also holds for convergence of stationary state wavefunctions and their gradients [39, 40]. In particular, for the 3D hydrogen-like atom in a sphere with large radius R , the lowest energy values are ordered in energy as follows:

$$1s, \{2p, 2s\}, \{3d, 3p, 3s\}, \dots \quad (2.5)$$

Here we use brackets to denote the groups of levels with the same limits as $R \rightarrow \infty$ [15, 17, 41]. For the spherically confined 3D isotropic harmonic oscillator, for large R values, the order of the states differs from (2.5) [21]:

$$1s, 1p, \{1d, 2s\}, \{1f, 2p\}, \{1g, 2d, 3s\}, \dots \quad (2.6)$$

It is difficult to find general statements on the energy spectrum for arbitrary potential. However it may be demonstrated for a wide class of potentials, including the Coulomb one, that for small enough cavity size the potential does not influence the state's ordering and in case of the Dirichlet problem the levels are in the same order as of the free particle in the same box. For the spherical cavity, the following order can be found [33]:

$$1s, 2p, 3d, 2s, 4f, 3p, 5g, 4d, 6h, 3s, \dots \quad (2.7)$$

(the hydrogen-like notations are used here, that is, $n \geq \ell + 1$, in contrast with Eq. 2.6).

2.2.2 The Cavity of the More Complex Form

For the system in a non-spherical cavity, one may expect the additional splitting of the energy levels that were degenerate for the free system. Application of perturbation theory methods would seem natural, but a caution should be addressed here. Let us consider the simplest case of a non-degenerate level, as the generalization to the case of degenerate level is rather obvious. When the effect of the finite potential walls of the height U_0 around the cavity Ω is described, one may introduce the perturbation of the form $U_0 \chi_\Omega^c(\mathbf{r})$, where χ_Ω^c is the characteristic function of the complement Ω^c of the region Ω in \mathbb{R}^3 . In the first order of the perturbation theory, one may write

$$E_j(\Omega, U_0) \approx E_j + U_0 \int_{\Omega^c(R)} |\psi_j(\mathbf{r})|^2 d\mathbf{r} \quad (2.8)$$

The exact energy levels $E_j(\Omega, U_0)$ are lower than the Dirichlet energies $E_j(\Omega)$ and converge to $E_j(\Omega)$ in the limit $U_0 \rightarrow \infty$ monotonically [40]. Unfortunately, relation (2.8) itself cannot describe this limit correctly, as the right hand side obviously diverges (recall that the ψ_j and E_j notations correspond to the free system, i.e. they are independent of U_0). Note that it was demonstrated in the classic work by Wigner [42] that perturbation theory requires carefulness when applied to the “box” problems. However, the use of such a perturbation for large R values seems to be useful at least for qualitative discussions. One may hope, that at least the state ordering may be estimated correctly for some finite U_0 value when Ω is large enough and the wavefunctions of the free system decrease exponentially. Note that it is a common situation that the radial functions of quantum mechanical problems may be asymptotically described as $Br^\eta \exp(-\alpha r^\beta)$ for some positive constants. All the calculations below will be performed within this supposition.

Let R be the distance from the potential center O to the boundary $\partial\Omega$, that is R is equal to the radius of the sphere with the center O inscribed in the cavity Ω . The sphere mentioned touches the boundary $\partial\Omega$ at points $\{\mathbf{r}_k\}$ ($|\mathbf{r}_k| = R$). Let us suppose, that any ray starting from the potential center crosses the boundary $\partial\Omega$ in exactly one point (for example, this is true for any convex region Ω). Then one may estimate the integral in Eq. (2.8) by the Laplace method (see Sect. 4.1–4.3 of [43]) for the radial variable. The resulting surface integral also may be evaluated by the Laplace method. A simple idea, but a very cumbersome calculation shows that the integral is reduced to the sum of the wavefunction values at the points $\{\mathbf{r}_k\}$. Hence for large enough R one may write

$$E_j(\Omega(R)) \approx E_j + \frac{\pi U_0}{2(\alpha\beta)^2} R^{3-2\beta} \sum_k |\psi_j(\mathbf{r}_k)|^2 \quad (2.9)$$

where α, β are the parameters of the above mentioned asymptotical form of the wavefunction ψ_j . The modification of these relations to the case of the degenerate level is now trivial. Nevertheless one may use Eq. (2.9) for the degenerate states when one component of a certain symmetry type is considered.

For us, these formulas are not interesting in themselves, but only as qualitative results that show that the values of the free problem wave functions at the points $\mathbf{r}_k(R)$ of $\partial\Omega$ determine the asymptotic behavior of the energy shifts.

2.2.3 Polyhedral Cavity

In the case of highly symmetrical cavities and the location of the potential origin at the center of symmetry, one may apply the standard group-theoretical methods

primarily developed in the framework of the Crystal Field Theory for the analysis of reduction of the rotational group of R^3 on a given subgroup (in this case—the symmetry point group of the cavity). For example, the splitting laws of states with the lowest values of the angular momentum are well known [27–29]. Thus one may note for the cubic or octahedral cavities (the symmetry group O_h) the following reduction laws

$$s \rightarrow a_{1g}, p \rightarrow f_{1u}, d \rightarrow e_g + f_{2g}, \dots \quad (2.10)$$

According to the conventional symmetry notations, the a -states are non-degenerate, while e - and f -states are doubly and triply degenerated, respectively. Note that sometimes O_h states of the f -type are denoted in literature as t .

Among the symmetry operations there is no inversion for the tetrahedral cavity (T_d). This is followed by more complex form of reduction. The symmetry type f_2 appears both for p and d -levels:

$$s \rightarrow a_1, p \rightarrow f_2, d \rightarrow e_g + f_2, \dots \quad (2.11)$$

Relations like (2.9) for energy shifts and levels splitting allow us to expect that the symmetry of the cavity Ω may be enough to determine the order of the splitted states. Unfortunately, this is not the case.

Let us consider some numerically calculated data for the hydrogen atom at the center of the impenetrable cubic cavity. Here we will not describe energy changes under the displacements of the nucleus away from the center (see the analysis in [44]). For the present calculations, we have used the method presented in [45] (see Sect. 2.3.3).

Let the vertices of the cube be truncated with conservation of the O_h symmetry of the cavity. This truncation may be described by the dimensionless parameter X that defines the proportion of the truncated edge from the side of each of vertices. The value $X = 0$ corresponds to the regular cube, while at $X = 0.5$ the cube edges disappear, and the truncated cube is the cuboctahedron. The same polyhedron is the result of truncation of the octahedron of the appropriate size. The results of truncation of the cube and the tetrahedron are jointly represented in Fig. 2.1. for the initial cube edge length of 4 au. As an abscissa, the variable t is used that defines the cube truncation when $t < 0.5$ by the relation $t = X$; for $t > 0.5$ we use the definition $t = 1 - X$, where X defines the octahedron truncation. The point $t = 1$ corresponds to the regular octahedron.

Note that for any truncated cube with $X \leq 0.5$, the inscribed sphere radius is the same and, based on relation (2.9), one could expect the conservation of the state ordering. The Fig. 2.1 shows that this is indeed the case. For the hydrogen atom in the spherical cavity with $R \approx 2$ au, the levels are ordered as $1s, 2p, 2s, 3d, \dots$ and the levels $2s$ and $3d$ are degenerated for $R = 2$. As it was explained, the compression that accomplishes the truncation of both cube and octahedron is followed by energy increase [38]. These details are well represented in Fig. 2.1.

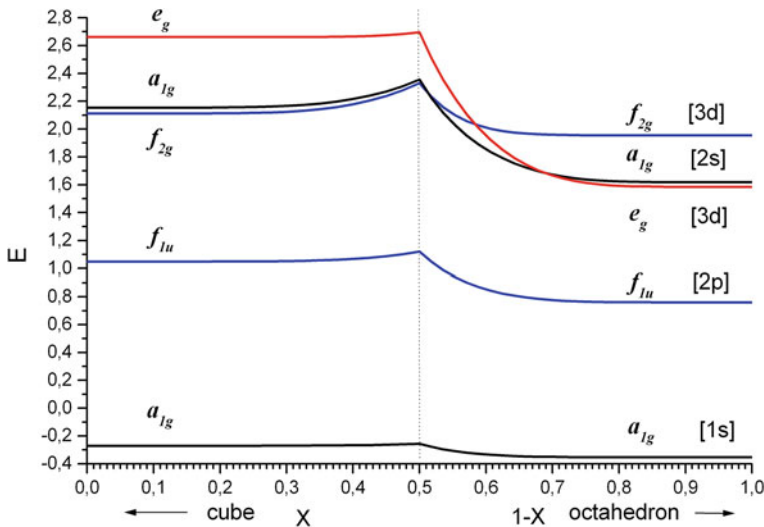


Fig. 2.1 Energy levels (au) for hydrogen atom placed at the centre of the cavity formed by joint symmetrical truncation of both the cube with the edge 4 au and the octahedron. For an explanation of the choice of dimensionless abscissa axis, see the text. In *brackets*, the corresponding states of the free atom are supplied

It is interesting that the most essential changes in the state ordering occur near the point $t \approx 0.58$ where the points of the cavity boundary closest to the center of the truncated octahedron replace that ones for the truncated cube. The relative position of the state a_{1g} [2s] changes near this point. When the size of the initial cube increases, the energies of the states decrease and the corresponding curve for the state $2a_{1g}$ is much closer to the state $1f_{1u}$ in accordance with the scheme (2.5). The intersection point for the states e_g and f_{2g} remains practically unchanged with the cavity size increase, and one may expect relations like (2.9) to be useful for similar considerations, though the positive U_0 value is undefined and the cavity size is small.

In a similar way change the energy values in other confined systems. For example, Fig. 2.2 demonstrates energies of an isotropic harmonic oscillator in a tetrahedral cavity truncated in a symmetric way into an octahedron. It is interesting that the qualitative behavior of the states for the harmonic oscillator is close to that of a hydrogen atom (one may compare Fig. 2.2 with the Fig. 6 of the work [45]). The position of the degeneracy point for the states e and f_2 varies essentially with the size of the tetrahedron and one can not use any simple geometrical arguments here.

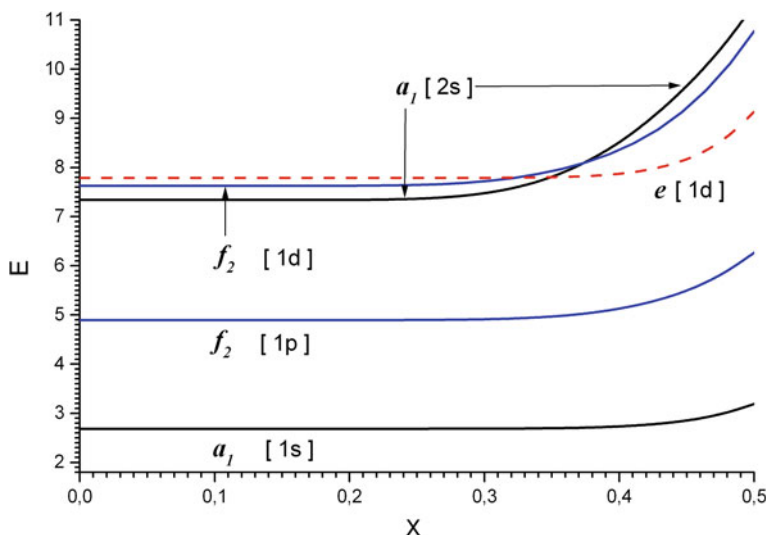


Fig. 2.2 The energies of the isotropic harmonic oscillator with the force constant $K = 1$ au placed at the center of the tetrahedral cavity with the edge 5.65 au ($X = 0$) truncated to octahedron ($X = 0.5$)

2.2.4 Note on the State Ordering

In certain cases, at least some of details of the state ordering can be explored by means of simple qualitative arguments. Let us consider the 3D isotropic harmonic oscillator with a variable force constant K in some fixed polyhedral cavity. When K is large enough, one may consider the system as being practically free (indeed, the wave functions of the lowest states are localized near the origin and the effect of the boundaries can be shown to be negligible [39]). In this limiting case, the states are ordered according to Eqs. (2.6), (2.10). When the force constant is negative-valued, there are no discrete spectrum states in the free system, but for the same system in an impenetrable cavity, only a discrete spectrum exists. It is quite clear that, in the latter case, the wave functions of the low lying states are localized near the vertexes of the polyhedral cavity. One may further consider conventional correlation diagrams to establish the state ordering in between the two limiting cases, $K \rightarrow -\infty$ and $K \rightarrow +\infty$.

For example, for a cubic cavity, it is quite evident that when $K < 0$ and $|K|$ is large enough, at least 8 lowest states may be adequately represented as proper linear combinations of 8 symmetry-equivalent basis functions, each being localized near one of the vertexes. The corresponding 8-fold representation of the point group O_h is easily decomposed into the following irreducible components: a_{1g} , a_{2u} , f_{1u} and f_{2g} . The fact that e_g -states are absent in this list implies that such states are situated much higher in energy. Therefore, in the study of the d-state splitting of the harmonic oscillator in a cubic cavity, in accordance with the symmetry reduction law

(2.10), it is natural to expect that the e_g -state is higher in energy than f_{2g} -state, at least for the 1d-level. For octahedral cavity, one may apply the same method to find that six localized states define the lowest states of the types a_{1g} , f_{1u} and e_g .

Note that one may use similar arguments for the Coulomb potential case. In this case one should use negative nuclear charges to construct the correlation diagram instead of negative K values for the case of harmonic oscillator. This difference is unessential for the method presented. In particular, this makes it clear the $e_g - f_{2g}$ state inversion when the cube is transformed into the octahedron (see e.g. Fig. 2.1). This is well known in the Crystal Field theory, though the state ordering on Fig. 2.1 differs from the usual one for the atomic states when the one-electron atom is surrounded by negatively charged ligands.

For the tetrahedral cavity, the constructions described above are practically useless, as for the tetrahedron the four lowest states are of the types a_1 and f_2 correlated with the free atomic states 1s and 2p. For example, one may find for the harmonic oscillator in a tetrahedral cavity with the edge 6.53 au, that the splitting of the harmonic oscillator 1d-state into $2f_2$ and e is inverted near the force constant value of $K \approx 1.5$ au. This example demonstrates that the real level splitting results from the interplay of numerous factors that require special attention and care.

2.3 Some Methods for Systems in Bounded Cavities

Practically each of the works on confined systems uses some original numerical method for the real states analysis. Here we describe only some of them, mainly important for qualitative description of the state order.

2.3.1 On the Numerical Methods for the Problems in the Sphere

The simplest way for solution of the confined system problem with the full spherical symmetry is the analysis of the radial wave functions $R_\ell(r, E)$ for a given angular momentum and arbitrary energy value E. For quantum-chemical problems, any acceptable solution should be bounded at the origin and therefore behaves like r^ℓ . The energy values of the stationary states with a given ℓ value for the Dirichlet problem within an impenetrable spherical cavity of radius R are defined by solutions of the following equation

$$R_\ell(R, E) = 0 \quad (2.12)$$

Radial functions and solutions of Eq. (2.12) may be determined analytically or numerically for any E values. Similar methods are used to study the systems in cavities like combinations of some spheres [46]. On the numerical methods for the

problem with fixed nucleus see [47]. For the use of the perturbation theory and other constructions see [41, 48, 49].

Of course, the finite difference calculations and combined methods are also used in practice. For example, a combination of numerical methods was implemented to describe both electronic and nuclear motion in the adiabatic approximation and to estimate the rovibronic energy levels and transition probabilities for the fully-dimensional problem of hydrogen atom in a spherical cavity [50]. Similar constructions were used for modeling of vibrational and rotational energy levels of diatomic molecules in an impenetrable sphere and to analyze the isotopic substitution effects in molecular spectra [51, 52]. Note also an interesting study of diatomics in cavity in [53, 54]. The methods for nuclear motion [55, 56] are closely related with methods for two-electron systems [57, 58].

The effective potentials for the cavity simulation also may be used. This makes it possible to use more traditional methods of quantum chemistry and molecular modeling, but this line is far from the subject of this text, though the techniques mentioned are developing rapidly in recent years.

2.3.2 The Method of Cutting Functions

It was suggested in [6] to consider the wave functions of the system in a cavity in the form $f(\mathbf{r})\psi(\mathbf{r})$, where ψ is some square-integrable solution of the Schrödinger equation for the problem in the whole space, and $f(\mathbf{r})$ is a “cutting factor”, which ensures fulfillment of the desired boundary conditions. For example, for the Dirichlet problem one may use functions with special property $f|_{\partial\Omega} = 0$ (it is supposed here that for $\mathbf{r} \notin \Omega$ one puts $f(\mathbf{r}) = 0$). At one time this idea was popular and often used for numerical estimates [59], for example, in the perturbation theory. For the history of the method and its applications see also [40, 60]. For the application of this technique to the confined system problems see [60–66].

Within the linear variational method, the use of cutting functions is particularly efficient. For example, when the boundary is not too curvy, one may calculate the matrix of the Hamiltonian in the basis of functions like $\{f\psi_j\}$ by using the sesquilinear form

$$\varepsilon(u, v) = \frac{1}{2} \langle \nabla u | \nabla v \rangle_{\Omega} + \langle u | V | v \rangle_{\Omega} \quad (2.13)$$

where the index Ω indicates the integration over the region only. Continuation of all the functions out of Ω by zero value allows omitting this index.

Note that when the function v is in the domain of definition of the Hamiltonian operator, then one may use the Green’s relation to find

$$\varepsilon(u, v) = \frac{1}{2} \int_{\partial\Omega} u \partial_n v d\sigma + \langle u | H v \rangle_{\Omega} \quad (2.14)$$

Here, u may be any piecewise smooth function and this property extends the possible class of cutting functions. For example, let f be the piecewise smooth function with properties $|f| \leq 1$ and $f = 0$ in Ω^c ; in particular, $f|_{\partial\Omega} = 0$. Let us use the wavefunctions ψ_m and φ_k for the free and the Dirichlet problems, correspondingly, to calculate the values $\varepsilon(f\psi_m, \varphi_k)$ and $\varepsilon(\psi_m, f\varphi_k)$ with the help of relation (2.14). One may find that

$$(E_k(R) - E_m) \langle f\psi_m | \varphi_k \rangle = \frac{1}{2} \int_{\Omega} (\nabla f, \psi_m \nabla \varphi_k - \varphi_k \nabla \psi_m) d\mathbf{r} \quad (2.15)$$

where (\cdot) means the inner product of 3D-vectors. The surface integrals are absent in this relation due to boundary properties of functions f and φ_k . One may note that the integrand in the right hand side of (2.15) is non-zero only in the region where the cutting function f differs from 1. Usually this region is some neighborhood of the boundary $\partial\Omega$. Sometimes one may suppose that in this neighborhood the functions φ_m and ψ_m are proportional and one may find the function $f = f_0$ such that for all the points where $\nabla f_0(\mathbf{r}) \neq 0$, one may write $\varphi_m(\mathbf{r}) = f_0(\mathbf{r})\psi_m(\mathbf{r})$ (in other points of Ω , where $f_0 = 1$, this relation may fail). For the function f_0 one may write (2.15) in the form

$$(E_m(R) - E_m) \langle f_0\psi_m | \varphi_m \rangle = \frac{1}{2} \langle \psi_m (\nabla f_0, \nabla f_0) \psi_m \rangle \quad (2.16)$$

The other important relation of this type is the Kirkwood-Buckingham relation [40] that may be written for any function $f(\mathbf{r})$ as

$$\begin{aligned} H_{mn} &= \varepsilon(f\psi_m, f\psi_n) \\ &= \frac{1}{2} (E_m + E_n) \langle \psi_m | f^2 | \psi_n \rangle + \frac{1}{2} \langle \psi_m | (\nabla f, \nabla f) | \psi_n \rangle \end{aligned} \quad (2.17)$$

In particular, for the finite set of N basis functions $f\psi_1, f\psi_2, \dots, f\psi_N$ one may compose the $N \times N$ Hamiltonian matrix \mathbf{H} with the elements H_{mn} and calculate the variational energy estimates for the Dirichlet problem in the region Ω . In recent years similar variational methods in the basis of cutting functions were often applied to many-electron systems; see, for example, [58]. The overlap matrix \mathbf{W} for the set $\{f\psi_j\}$ has the form $\mathbf{W} = \mathbf{1} - \mathbf{Q}$ where \mathbf{Q} is the matrix with elements $Q_{ij} = \langle \psi_i | 1 - f^2 | \psi_j \rangle$. It is important here that the matrix \mathbf{Q} is nonnegatively defined when $|f| \leq 1$. In particular, its largest eigenvalue does not exceed the trace of \mathbf{Q} .

The generalized eigenvalue problem with the Hamiltonian matrix \mathbf{H} and the overlap matrix \mathbf{W} gives upper bounds E_j^* for the exact energies $E_j(\Omega)$ (“the Hylleraas-Undheim-MacDonald theorem” [67]). Hence the sum of N lowest

energies $E_j(\Omega)$ is estimated by the sum of N numbers E_j^* . The standard method allows to estimate the sum:

$$\sum_{j=1}^N E_j(\Omega) \leq \sum_{j=1}^N E_j^* = \text{tr} \mathbf{H} \mathbf{W}^{-1} \quad (2.18)$$

Due to relations (2.17) for the matrix elements, it is easy to rewrite this inequality in the form

$$\sum_{j=1}^N (E_j(\Omega) - E_j) \leq \frac{1}{2} \left(\sum_{j=1}^N \langle \psi_j | |\nabla f|^2 | \psi_j \rangle \right) / (1 - \text{tr} \mathbf{Q}) \quad (2.19)$$

where $1 - \text{tr} \mathbf{Q}$ gives the lower bound for the lowest eigenvalue of the overlap matrix \mathbf{W} . Of course, it is supposed in inequality (2.19) that the $\text{tr} \mathbf{Q}$ is small enough.

All the terms in the sum in the left hand side of Eq. (2.19) are positive numbers only and one may estimate each of the energy differences by the right hand side of this relation. We will use Eq. (2.19) below. An alternative way to derive Eq. (2.19) is presented in [39].

2.3.3 The Cavity of the More Complex Form

The main problem with cavities of a complex form is the compact description of the cavity boundary surface. When the surface $\partial\Omega$ is not too complex one may use the method described in [45], similar to the Shooting Method for 1D problems: for one-electron problems one may define the energy values by imposing the boundary conditions on the trial function $\varphi(\mathbf{r}, E)$. Here $\varphi(\mathbf{r}, E)$ is a solution of the differential Schrödinger equation for some trial energy value E . For example, for the spherically symmetric potential, the radial functions $R_\ell(r, E)$ are known analytically or numerically. For low symmetry cavities, one may construct the functions of a definite symmetry type Γ as linear combinations $Y_\ell^{(\Gamma)}(\theta, \varphi)$ of spherical harmonics with some appropriate ℓ values. Thus the functions $u_\ell(\mathbf{r}, E)$ of the form $R_\ell(r, E) Y_\ell^{(\Gamma)}(\theta, \varphi)$ may be considered as a basis set for determination of a trial function of the form

$$\varphi^{(L)}(\mathbf{r}, E, \mathbf{c}) = \sum_{\ell=0}^L c_\ell u_\ell(\mathbf{r}, E) \quad (2.20)$$

Later on we use the \mathbf{c} symbol for the vector with coefficients $\{c_\ell\}$. The (2.20) define some solution of the Schrödinger equation for each energy E and vector \mathbf{c} for a given symmetry species. For normalized functions $\varphi(\mathbf{r}, E, \mathbf{c})$ the Dirichlet boundary condition (2.3) can be replaced with the relation $D(\varphi, E, \mathbf{c}) = 0$, where the functional D is defined as

$$D(\varphi, E, \mathbf{c}) = \int_{\partial\Omega} |\varphi(\mathbf{r}, E, \mathbf{c})|^2 d\sigma \quad (2.21)$$

This is the qualitative idea of the method described. It is based on the statement, that when for some functions $\varphi^{(L)}(\mathbf{r}, E^{(L)}, \mathbf{c}^{(L)})$, being solutions of the differential Schrödinger equation, for $L \rightarrow \infty$ one may state that $\{D(\varphi^{(L)}, E^{(L)}, \mathbf{c}^{(L)})\} \rightarrow 0$ and $E^{(L)} \rightarrow E_*$, then the limiting value E_* defines the point of the discrete spectrum of the Hamiltonian (2.1) with the Dirichlet boundaries. This is not a trivial statement but restrictions on the functions $\{\varphi^{(L)}\}$ are not too strong; see [45].

When one tries to minimize the functional D (2.21) with trial functions of the form (2.20) with respect to the vector \mathbf{c} , it is clear that the quadratic form optimization results in a generalized eigenvalue problem

$$\Sigma \mathbf{c} = \delta^{(L)}(E) \mathbf{S} \mathbf{c} \quad (2.22)$$

where \mathbf{S} is the usual $L \times L$ overlap matrix for the basis functions $\{u_\ell\}$, calculated by integration over the region Ω , while Σ is a similar overlap matrix, but for the restrictions of the functions $\{u_\ell\}$ only to the surface $\partial\Omega$. The vector \mathbf{c} defines optimal approximation for $\varphi^{(L)}$, while the lowest eigenvalue $\delta^{(L)}(E)$ gives the optimal value of the functional for a given energy value E .

When the function $\delta^{(L)}(E)$ is known, one may find the set of its local minima $E_1^{(L)}, E_2^{(L)}, \dots$ with respect to E . These local minima define, with increasing L , the estimates for the energy levels $E_1(\Omega), E_2(\Omega), \dots$ for the Dirichlet problem. The L values required for calculations of low lying states are usually not too large.

There exist a variety of realizations of the idea described. One may note that when there exists a zero eigenvalue of the matrix Σ , then it is the solution of Eq. (2.22) for any form of the matrix \mathbf{S} . In particular, in order to optimize the calculation time, one may use approximate forms of the matrix \mathbf{S} ; this is equivalent to the use of some weights for calculation of the functional D . For example, one may use the diagonal part of \mathbf{S} only, or $\mathbf{S} = 1$. Of course, the results are stable to such modifications only when the optimal values of $\delta^{(L)}(E)$ are small enough. For example, in [45] we used the exact \mathbf{S} matrix, while in [44, 68] simpler forms of overlap matrices were also tested. Note that the complete form of the method gives the most stable computational results. The numerical data used for Figs. 2.1 and 2.2 were prepared by this method.

Note that for the spherical cavity Ω , the described method is simplified and reduces to the usual solution of Eq. (2.12), and one may consider the construction described as “the Shooting Method”. One may use both analytical and numerical estimates for radial functions. One may consider the integral D minimization as looking for approximate solution of the problem $\varphi^{(L)}|_{\partial\Omega} = 0$ at some grid points. So one may consider the method as a variety of the Least Squares Method with weights or as the collocation method.

For the excited states, the stability of the method decreases and it is sensitive to the choice of the grid points used for calculations. The search of local minima for

$\delta^{(L)}(E)$ function becomes a very difficult problem as the minima are too sharp for large L values. Nevertheless, when compared with other numerical tools such as finite difference, perturbational or variational approaches [48, 49], the present methods are quite reliable. In particular, they may be used for other types of boundary value problems like Eq. (2.4).

2.4 Cavities of the Large Size

2.4.1 Evaluation of the Energy Shift

Let us evaluate the energy shift for a system in an impenetrable cavity with respect to the free system. There exist a number of ways to do it. In any case, we consider a parametric family of cavities expanding with the parameter growth. As a parameter mentioned, the radius R of an inscribed sphere with the centre at the origin of the potential is convenient. It is possible to prove L_2 convergence of the wavefunctions $\varphi_j(\mathbf{r}, \Omega(R))$, continued as identically zero-valued outside $\Omega(R)$, to the solutions $\psi_j(\mathbf{r})$ of the free problem. For 1D or equivalent problems it was first demonstrated in [69] with Ω being a sphere. A similar in spirit but different in realization approach developed in [70, 71] allows to asymptotically estimate the energies, wave functions, oscillator strengths and polarizabilities for the confined hydrogen atom in selected states. Some analytical approaches were also developed in [72–76]. (However, the detailed theoretical description of the R -dependence for oscillator strength of the hydrogen atom, estimated in the wide range of the spherical cavity radii in [77], does not exist up to now.)

The convergence of the energy levels $E_j(R)$ to E_j is almost evident. For example, one may use the cutting function f that differs from 1 in a neighborhood of $\partial\Omega$ for points $|\mathbf{r}| > \gamma R$ where $\gamma < 1$ is fixed. The function f decreases to zero value at $\partial\Omega$. As it was already mentioned, we use the asymptotic form $Br^n \exp(-\alpha r^\beta)$ for the radial parts of the free problem wavefunctions (this idea was proposed in [69]). It is obvious in this case, that the $\langle \psi_k | (1-f^2) | \psi_k \rangle$ integrals converge to zero exponentially. Hence one may use inequality (2.19) in the form

$$\sum_{j=1}^N [E_j(R) - E_j] \leq \frac{1}{2} \sum_{j=1}^N \langle \psi_j | |\nabla f|^2 | \psi_j \rangle (1 + o(R)) \quad (2.23)$$

with some positive function $o(R)$ that vanishes exponentially. As the integrals in this relation are calculated for the region $|\mathbf{r}| > \gamma R$, the right hand side of Eq. (2.23) also converges to zero when $|\nabla f|$ is bounded.

One may rewrite (2.23) in a simpler form. It is a usual situation that the rate of decay of discrete energy spectrum wave functions at infinity decreases with the excitation level. Hence, for a non-degenerate energy level, one may write the following asymptotic relation for large enough R values and $|\mathbf{r}| > \gamma R$:

$$\sum_{j=1}^N |\psi_j|^2 \cong |\psi_N|^2 \quad (2.24)$$

and one may rewrite (2.23) in a much weaker form

$$E_N(R) - E_N \leq \frac{1}{2} \left\langle \psi_N || \nabla f|^2 | \psi_N \right\rangle (1 + o(R)) \quad (2.25)$$

Relations of this kind may be used to prove convergence of wavefunctions and their gradients [39] by means of a combination of the Eckart relations [78] and the Katriel trick [79]. Alternatively, this can be established by virtue of the Löwdin's results (see (3.41) in [80]).

More refined approval can be obtained if one uses (2.16) with some appropriate function f_0 . This is true, for example, in one-dimensional problems or for the radial equation, when for a sufficiently large distance from the centre, the potential values are higher than the energy studied. It follows from the bilateral estimate $0 \leq f_0 \leq 1$ and the convergence of $f_0 \psi_m$ to φ_m with increasing R , that the integrals $\langle f_0 \psi_m | \varphi_m \rangle$ converge to 1, not exceeding 1. Hence one may estimate the energy shift from below, as follows:

$$E_m(R) - E_m \geq \frac{1}{2} \left\langle \psi_m || \nabla f_0|^2 | \psi_m \right\rangle \quad (2.26)$$

Relations (2.25) and (2.26) are similar, but obviously not equivalent. However, in the problems that may be reduced to one-dimensional ones, one may look for the optimal form of the function f from the minimization of the integral in the right hand side of (2.25) (see e.g. Sect. 4.4 in [16]). As simple estimates show, with optimal choice of $f = f_{\text{opt}}$, the leading asymptotic term essentially depends on the behavior of the wave functions at the boundary only, and this circumstance allows us to combine estimates (2.25) and (2.26) in the case of spherical regions. The energy shift is evaluated asymptotically through the radial part of the wave function of the corresponding state of the free problem (here and later we use the radial functions that are normalized with the weight factor r^2):

$$\begin{aligned} E_m(R) - E_m &\cong \frac{1}{2} \left\langle \psi_m || \nabla f_{\text{opt}}|^2 | \psi_m \right\rangle \\ &\cong -r R_m(r) \partial_r [r R_m(r)]|_{r=R} \cong -R^2 R_m(R) \partial_r R_m(R) \end{aligned} \quad (2.27)$$

Here, the symbol ∂_ξ is used for the derivative with respect to the variable ξ . The same estimate was described in [69]. For the next asymptotic terms of the energy shift, see [70, 71, 81].

2.4.2 The Large Polyhedral Cavity

For regions of general type we cannot guarantee the relations like (2.26) to be true, but one may suppose the estimates of the form (2.25) to be not too poor. The optimal form of the cutting function in Eq. (2.25) for convex polyhedral cavities (or cavities described in Sect. 2.2.2) may be estimated by a solution of a pair of one-dimensional problems. We will not give here fairly cumbersome intermediate stages of asymptotic calculations, leading to qualitatively clear relations.

The upper bound for the optimal integral $\langle \psi_m | |\nabla f^*|^2 | \psi_m \rangle$ value can be found if one uses the functions $f(\mathbf{x})$ specified only by the distance from the point \mathbf{x} to the nearest plain face of the polyhedron. This is the case when one may reduce the three-dimensional integrals to one-dimensional ones using the density of the state averaged over the planes parallel to the polyhedron faces. All the calculations may be performed on the basis of the method of Laplace (see Sects. 4.1–4.3 of [43]) for the wave functions ψ_m of the above mentioned form.

For the polyhedron, the lower bound for the optimal integral value can be also found when optimizing the cutting function along the radial direction from the center to the boundary and omitting all the angular contributions in $|\nabla f|^2$. The remaining integral over the angular variables is calculated again using the method of Laplace.

It is interesting that the leading terms of asymptotic expansions for the integral under consideration are the same for both the upper and lower bounds, and the resulting asymptotical value of the integral is expressed through the points $\{\mathbf{r}_k\}$ where the inscribed sphere touches the faces of the polyhedron (see also Sect. 2.2.2). Thus one may write for $R \rightarrow \infty$

$$\frac{1}{2} \langle \psi_m | |\nabla f_{\text{opt}}|^2 | \psi_m \rangle \cong 2\pi R \sum_k |\psi_m(\mathbf{r}_k)|^2 \quad (2.28)$$

This estimate differs from the perturbation theory result (2.9) by a radial factor only, but the factor does not change the state ordering, according to Eqs. (2.9) or (2.28). So the role of the points $\{\mathbf{r}_k\}$ in evaluating the energy shifts is confirmed in an independent way.

The modification of Eq. (2.28) for the degenerate case is almost trivial. For example, let us consider the splitting of the degenerated energy level of hydrogen atom with the given principal quantum number n . The free atom radial wave functions have the form $r^{n-1}e^{-r/n}$ at large distances from the nucleus, and they differ in the numerical factors $B_{n\ell}$ only [33]:

$$B_{n\ell} = \frac{2^n}{n^{n+1} \sqrt{(n+\ell)!((n-\ell-1))!}} \quad (2.29)$$

If one is interested in the state ordering, the radial contributions may be omitted and the splitting of the states with respect to the exact free atom value $E_n = -1/2n^2$

Table 2.1 The energy splitting (t_k in relative units) of the hydrogen atom states with $n = 3$ in some large polyhedral cavities

Polyhedron	Assignment and t_k			
O_h	$1f_{2g}$	$1e_g$	$2f_{1u}$	$3a_{1g}$
Cube	0	0.97	1.94	3.88
Octahedron	0.86	0	2.59	5.17
T_d	$2f_2$	$1e$	$3f_2$	$3a_1$
Tetrahedron (3s, 3p, 3d)	0	0	1.72	2.59
Tetrahedron (3d)	0.43	0	–	–

is defined by eigenvalues $\{t_j\}$ of the matrix \mathbf{T} defined as follows. The matrix elements of \mathbf{T} are expressed through the B-factors (2.29) and the values of the spherical harmonics at the respective points $\{\omega_k = \mathbf{r}_k/R\}$ on a unit sphere:

$$T_{i,j} = B_{n\ell_i} B_{n\ell_j} \sum_k Y_i(\omega_k) Y_j(\omega_k) \quad (2.30)$$

For some classical polyhedra, the calculated energy splittings for $n = 3$ are collected in Table 2.1.

Recall that for the hydrogen-like atom in a large spherical cavity the levels with the principal quantum number $n = 3$ are ordered as 3d, 3p, 3s. This is consistent with the data from Table 2.1, where the 3p and 3s levels are referred to as $(2f_{1u}, 3a_{1g})$ and $(3f_2, 3a_1)$ for cubic and tetrahedral systems, respectively. For the case of the tetrahedron, the reduction laws (2.11) make it possible to consider also the splitting of 3d states, also presented in Table 2.1.

Note, however, that for the tetrahedron in the case $n = 3$, the 5-fold degeneracy conserves within the leading asymptotic order. The rank of the matrix \mathbf{T} is small (it equals 4) and the splitting of the 3d levels has to be studied in the next orders of the asymptotic expansion. In [45] we mention too small energy gap between $1e$ and $2f_2$ states originated from the 3d atomic levels in tetrahedral cavities even of relatively small sizes. For our discussion it is sufficient to notice that the small splitting of these levels makes them very sensitive to a variety of other factors that can be seen from discussion at the end of Sect. 2.2.4.

It is also worth noting that (2.28) and (2.9) look naturally in the context of the method presented in Sect. 2.3.3 (see Eq. 2.21). There exists an intrinsic relation between the energy shifts or splittings and the behavior of the free system wave functions at the boundary.

2.4.3 Wave Functions Near the Boundary

One may find a large number of different relations for the energy shifts. For example, one may estimate the value $\varepsilon(\psi_j, \varphi_j)$ as it was described in Sect. 2.3.2. The resulting relation was known to Fröhlich [6] and later it was re-derived many times:

$$(E_j(\Omega) - E_j) \langle \psi_j | \varphi_j \rangle_\Omega = -\frac{1}{2} \int_{\partial\Omega} \psi_j \partial_n \varphi_j d\sigma \quad (2.31)$$

In particular, one may note that for spherical cavities Ω the size increase is accomplished by convergence of $\langle \psi_j | \varphi_j \rangle_{\Omega(R)}$ to 1. Let us denote as $R_j(r|R)$ the radial parts of eigenfunctions of the Dirichlet problem normalized over the sphere with the weight factor r^2 . Then (2.31) is immediately followed by the asymptotic relation

$$E_j(R) - E_j \cong -\frac{1}{2} r^2 R_j(r) \partial_r R_j(r|R)|_{r=R} \quad (2.32)$$

This equation is close to (2.27) where only free problem functions $R_j(r)$ are used. The detailed comparison of (2.27) and (2.33) clearly demonstrates an interesting relation, that was found in [73] on the basis of analysis of explicit asymptotic relations for radial functions. For the Dirichlet problem, one may write that the following asymptotic relation holds in the $R \rightarrow \infty$ limit:

$$\partial_r R_j(r|R)|_{r=R} \cong 2 \partial_r R_j(r)|_{r=R} \quad (R \rightarrow \infty) \quad (2.33)$$

It is interesting that, for numerical estimates, Fröhlich used in [6] (see p. 946 near Eq. 6) the natural analog of this relation without the factor 2. The nature of this multiplier is clear from the simplified model that illustrates the discussion of [73]. Suppose that the Schrödinger equation has two solutions, one of which $R(r)$ decreases exponentially, while the other one grows exponentially. For large R values, one may write the solution of the Dirichlet problem in the form

$$R(r|R) \approx C[\exp(-\alpha r) - \exp(-2\alpha R) \exp(+\alpha r)] \quad (2.34)$$

The coefficient C is defined by normalization condition and may be thought to be a constant. The coefficient at the growing exponent is defined by the Dirichlet condition at the point R . It is evident that relation (2.33) holds indeed, as:

$$\partial_r R(r|R)|_{r=R} \approx 2C[-\alpha \exp(-\alpha R)] \approx 2 \partial_r R(r)|_{r=R} \quad (2.35)$$

Surprisingly, although the convergence of the sequence of energies and the norm-convergence of functions is insufficient to ensure the pointwise convergence for the functions or their derivatives, and such groundless conclusions are dangerous (see, e.g. (2.33) as an example, or [82, 83]), relation (2.33) may be obtained by using the optimal cutting function (see the text before Eq. 2.27).

For the hydrogen atom in a spherical cavity, asymptotics of wave functions are known. The use of estimates for the radial functions from [41, 71] immediately gives the following asymptotic relations

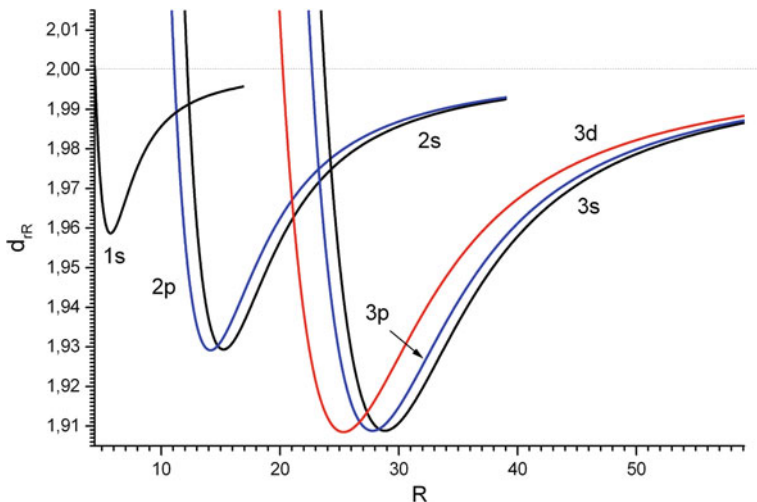


Fig. 2.3 The ratio of derivatives $d_{rR}(R)$ for radial wave functions of the hydrogen atom in the spherical cavity at the point $r = R$ (au)

$$d_R(R) = \frac{\partial_r R_{1s}(r|R)}{\partial_r R_{1s}(r)} \Big|_{r=R} \cong 2 - \frac{2}{R} + \dots \quad (2.36)$$

$$d_{rR}(R) = \frac{\partial_r [r R_{1s}(r|R)]}{\partial_r [r R_{1s}(r)]} \Big|_{r=R} \cong 2 - \left(\frac{1}{R^2} + \frac{5}{R^3} + \dots \right) \quad (2.37)$$

Clearly, ratio (2.37) for the functions normalized with a unit weight seems to be more accurate for relatively small values of R . But even for the region $R \sim 10$ au, where the 1s-state wave function practically vanishes, both d_R and d_{rR} values are markedly different from 2. This is evident from the numerical representation of these ratios, presented in Fig. 2.3. Interestingly, the results of numerical estimations of the derivatives at the boundary are close to the relations presented for $R > 7$ au. Note that, in accordance with the energy ordering, among a group of states with the same principal quantum number value, the higher the angular momentum, the faster the limiting value 2 is approached.

For the case of general boundary conditions one may repeat all the calculations on the basis of energy estimates from [16]. For example, for the Neumann conditions (2.2) for $R \rightarrow \infty$ one may state that $R_j(r|R)|_{r=R} \cong 2R_j(r)|_{r=R}$ [73].

2.5 Deformation of the Cavity of Large Size

2.5.1 The Basic Relations

Some almost obvious conclusions on the relative position of the energy levels of simple systems can be derived using the results for the spherical cavity. Let us consider the Dirichlet problem for cavities $\Omega(\lambda)$ that deform with the parameter λ changes. Let the point $\lambda = 0$ correspond to $\Omega(0) = \Omega$. The orthonormalized wavefunctions for the region $\Omega(\lambda)$ are denoted as $\varphi_k(\lambda)$; for $\lambda = 0$ we use the standard notations $\Omega(0) = \Omega$ and φ_k .

Differentiation of the identity

$$\varepsilon(\varphi_j, \varphi_k(\lambda)) - E_k(\Omega(\lambda)) \langle \varphi_j | \varphi_k(\lambda) \rangle = 0 \quad (2.38)$$

with respect to the parameter λ gives immediately (by using the Green's formula) a simple relation that may be written for $\lambda = 0$ as follows:

$$\begin{aligned} \partial_\lambda E_k(\Omega) \langle \varphi_j | \varphi_k \rangle &= \\ &= \frac{1}{2} \int_{\partial\Omega} \partial_n \varphi_j \partial_\lambda \varphi_k d\sigma + [E_j(\Omega) - E_k(\Omega)] \langle \varphi_j | \partial_\lambda \varphi_k \rangle \end{aligned} \quad (2.39)$$

where the symbols $\partial_\lambda \varphi_k$ and $\partial_\lambda E_k(\Omega)$ denote the derivatives $\partial_\lambda \varphi_k(\lambda)$ and $\partial_\lambda E_k(\Omega(\lambda))$ at the point $\lambda = 0$. One may suppose that, under small deformation of the cavity, the point $\mathbf{z} \in \partial\Omega$ moves in the direction of the outer normal \mathbf{n} to $\partial\Omega$ at the point \mathbf{z} and transforms to the point $\mathbf{z} + \rho(\mathbf{z})\mathbf{n}d\lambda$. Then differentiation of the Dirichlet condition $\varphi_k(\mathbf{z}(\lambda), \lambda) = 0$ at the point $\lambda = 0$ allows one to estimate

$$\partial_\lambda \varphi_k = -\rho \partial_n \varphi_k \quad \text{for } \mathbf{z} \in \partial\Omega \quad (2.40)$$

(see the details, e.g. in [72] or [16]). Hence the orthogonality of the functions φ_k implies the simple relation

$$\partial_\lambda E_k \delta_{jk} = -\frac{1}{2} \int_{\partial\Omega} \rho \partial_n \varphi_j \partial_n \varphi_k d\sigma + [E_j(\Omega) - E_k(\Omega)] \langle \varphi_j | \partial_\lambda \varphi_k \rangle \quad (2.41)$$

Note that the functions $\{\varphi_k\}$ in (2.41) are *the limits* of the functions $\{\varphi_k(\lambda)\}$ when $\lambda \rightarrow 0$. It means, for example, that for an *arbitrary* set of M degenerated functions with the same energy one has to calculate the $M \times M$ matrix \mathbf{G} with the elements

$$G_{jk} = -\frac{1}{2} \int_{\partial\Omega} \rho \partial_n \varphi_j \partial_n \varphi_k d\sigma \quad (2.42)$$

and diagonalize it to find the derivatives $\partial_\lambda E_k$ as eigenvalues of the matrix \mathbf{G} ; the corresponding eigenvectors define linear combinations for which Eq. (2.41) holds. (Similar constructions are usual for perturbation theory for degenerate energy levels. Here is one of variants of such constructions).

Relation (2.41) in a slightly modified form is described in a large number of works, for example, [6, 84]. Note that for degenerate states, the second term in Eq. (2.41) vanishes.

2.5.2 Example: Expansion of a Spherical Cavity

For a large enough spherical cavity, one may use relations of Sect. 2.5.1 in combination with the asymptotical relations (2.33). For example, one may consider the expansion of the spherical cavity using R as the parameter. It is clear that the normal derivative to a sphere is the derivative with respect to the radial variable. Orthogonality of the spherical harmonics means that for a degenerate set of states with a given angular momentum one may write (see the text near Eq. 2.29)

$$\partial_R E_{n\ell} \cong G_{n\ell, n\ell} \cong -\frac{2}{n^2} B_{n\ell}^2 R^{2n} e^{-2R/n} \quad (2.43)$$

In agreement with Eq. (2.27), this relation is followed by

$$E_{n\ell}(R) = E_{n\ell}(\infty) - \int_R^\infty \partial_r E_{n\ell}(r) dr \cong E_{n\ell} + \frac{B_{n\ell}^2}{n} R^{2n} e^{-2R/n} \quad (2.44)$$

In particular, it is clear that the $B_{n\ell}$'s (2.29) define the state ordering in large cavities. The higher the ℓ , the smaller is $B_{n\ell}$. That is, the atomic states are ordered according to the decrease of the angular momentum (see Eq. 2.5). This statement is popular in the literature and may be explained by a variety of arguments [17, 41, 81]. It is presented here to explain the main ideas of the next subsections.

2.5.3 Asymptotically Degenerate States

When one considers the deformation of a very large cavity, relation (2.41) deserves more careful treatment. For example, for the hydrogen atom one has to consider the whole group of the asymptotically degenerate states with the same principal quantum number. Only for the case considered in Sect. 2.5.2 may one analyze states with different angular moments in the independent way due to the spherical symmetry of the problem.

When Ω is a sphere (or a slightly deformed sphere) of large radius R , one may use relations (2.33) to see that the contribution of the matrix \mathbf{G} in the right hand side of Eq. (2.41) is of the same order as the energy shifts or their derivatives. But there exists one more term in the right hand side of this equation. The energy difference $E_j(\Omega) - E_k(\Omega)$ vanishes for the states corresponding to the strictly degenerate energy level, but for a large enough region Ω this difference has the same order as the energy shifts and one may suppose it to be of approximately the same order as the energy shifts under consideration. This means that in the general case, one has to consider all the terms in Eq. (2.41).

In general, it is difficult to describe all the features of the wave function changes under deformations of the cavity. But it is possible when the states studied are localized mainly near the potential center, while the main changes in the densities are localized near the boundary. The examples of optimal cutting functions for similar problems [16, 39] confirm this statement. One may suppose the essential changes in $\partial_\lambda \phi_k$ mainly in the region $|r| > \gamma R$, for some linear size R of the cavity. It means that one may suppose that for large enough cavity size, the matrix elements $\langle \phi_j | \partial_\lambda \phi_k \rangle$ are small and decrease to zero with the cavity extension. But this is the case when the last term in the right hand side of Eq. (2.41) vanishes asymptotically in comparison with the first term.

For the situation considered one may reduce the derivative calculations to evaluation of the \mathbf{G} matrix for *all* asymptotically degenerate states. For example, for the one-electron atom, one should calculate the matrix \mathbf{G} in the basis of the states ns , np , nd , ... simultaneously. Nevertheless, it is difficult to exclude situations when the splitting of the states with different angular momenta is essential and it is desirable to consider also the splitting of the states with a given angular momentum separately.

2.5.4 The Polyhedral Deformation of the Sphere

Now we are ready to study the state ordering for the polyhedral deformations of the large spherical cavity Ω of radius R . We consider the set of similar polyhedrons $P(x)$ with the same center and parallel faces. The dimensionless parameter x describes extension of polyhedrons from inscribed in the sphere (for $x = 0$) to circumscribed around the sphere Ω (for $x = 1$). One may define the set of regions $\Omega^*(x) = \Omega \cap P(x)$ that may be considered as polyhedrons with vertices smoothed by the sphere or as a result of the “polyhedral” truncation of the sphere.

It would be interesting to analyze the changes in the hydrogen atom spectrum for the nucleus placed in the centre of an impenetrable cavity $\Omega^*(x)$. But we cannot use explicit relations for wavefunction derivatives on $\partial\Omega^*(x)$ and solve here another problem that may be considered as the sphere deformation “in the direction of the region $\Omega^*(x)$ ”.

For a pair of points $\mathbf{z} = R\mathbf{m}$ on $\partial\Omega$ and $\mathbf{z}^* = Rq(\mathbf{m}, x)\mathbf{m}$ on $\partial\Omega^*(x)$ we consider the deformation family $\Omega(\lambda, x)$ by the relation $\mathbf{z}(\lambda) = (1 - \lambda)\mathbf{z} + \lambda\mathbf{z}^*$ for the boundary $\partial\Omega(\lambda, x)$. It means that, in relations (2.40)–(2.42), one may use the function

$$\rho(\mathbf{z}) = R(q(\mathbf{m}, x) - 1) = R\rho_0(\mathbf{m}, x) \quad (2.45)$$

In order to calculate the matrix elements of \mathbf{G} (see Eq. 2.42) for the hydrogen atom, it is sufficient to use ρ_0 and spherical harmonics Y_k only. The radial functions are the same and may be omitted to analyze the energy level splitting (it may be considered as the use of a specific scale). That is, for each x we calculate the matrix Λ with elements defined as

$$\Lambda_{kj} = -B_{n\ell_k} B_{n\ell_j} \int Y_k^* Y_j \rho_0(\mathbf{m}, x) d\omega \quad (2.46)$$

The energy derivatives (2.41) are proportional to the eigenvalues Λ_j of this matrix.

It is clear that, due to relation $\Omega^*(x) \subseteq \Omega$, the energy derivatives with respect to λ are nonnegative. When the energy levels for large enough region Ω are considered as degenerate or almost degenerate, it is clear that the bigger the derivative Λ_j , the higher is the energy of the corresponding atomic state.

The results of the $e - f_2$ splitting in derivatives that may be attributed to the components of the 3d-state are presented for the hydrogen atom in Fig. 2.4 for different cavities $\Omega^*(x)$. We consider the families of the cavities defined by classical polyhedrons: cube, octahedron and tetrahedron.

Recall that, in the case of the cavities of the symmetry type O_h [cube, octahedron and associated families $\Omega^*(x)$], there exists parity that distinguishes the 3d and 3p

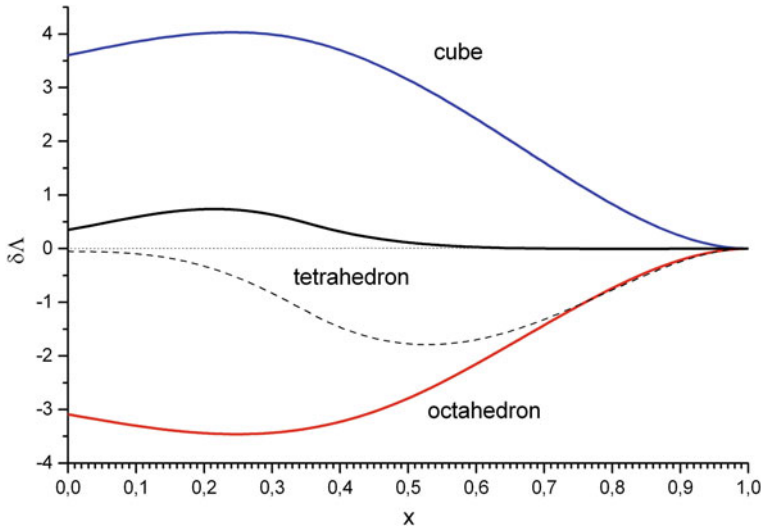


Fig. 2.4 The differences $\delta\Lambda = \Lambda(e) - \Lambda(f_2)$ for the sphere deformations “in the direction $\Omega^*(x)$ ” in relative units. The *solid lines* describe the difference for the system of states $\{3s, 3p, 3d\}$; the *dashed line* corresponds to the pure 3d-state in the tetrahedral family of cavities

states. But for tetrahedral systems, there is an essential difference between the splitting in the case of almost-degenerate 3s, 3p, 3d states and selected 3d states. As is clear from the Fig. 2.4 the interaction with 3p states drastically changes the splitting of the atomic 3d state and sometimes it is negligible. This observation can also be tied with the conclusions made on the basis of asymptotic estimates in Sect. 2.3 (see also Table 2.1 and the end of Sect. 2.1). Crudely speaking, for the 3d state, the levels are ordered in tetrahedral case so that the e level is below the f_2 one, but the 3p state of the same type f_2 shifts the lowest f_2 state below the e level.

One should stress the similarity of Eqs. (2.30) and (2.46), especially for the region $x \approx 1$.

2.6 Further Insights

Discussion of the problems of the relative positions of the energy levels of atomic and molecular systems in cavities of different types stimulates a lot of further insights of interaction between the system and the environment. The most serious problems here are those concerning the structured nature of the surrounding medium. This area is developing nowadays especially rapidly. In this regard, more sophisticated models were formulated, based on the use of systems of point charges or distributed multipoles, also taking into account the effects of polarization and short-range interactions [85]. One could also mention different embedded cluster and periodic models for a localized inhomogeneity in an extended medium which are increasingly used in practice, especially within the Density Functional Theory (DFT) framework. See, e.g. the comprehensive reviews [86, 87] and references therein for further details.

However, even in the simplest one-electron models new effects arise, e.g. when considering a potential model with finite height walls. For example, in the case of the hydrogen-like system in a cylindrical cavity, there were cases when the wave functions were pushed out of the too-small potential well [88]. It is interesting to note that similar effects occur in many-electron atoms [89] because the behavior of the wave functions inside and outside of the potential well in the field of the other electrons is considerably different [90].

Another kind of serious problems is associated with displacement of the atomic nucleus or other force center away from the highly-symmetric position in the cavity. Qualitative methods for this sort of problems were described, in particular, for cavities of small size, for spherical cavities [48], for cylindrical cavities [68, 91], for cubic [44], tetrahedral and similar cavities [45]. On the methods useful for icosahedral systems, see [92].

Many years ago [93–95] the energy changes were estimated for the hydrogen nucleus shifted from the center to the points of the cavity boundary for the quantum wire of square section. In this case, the results are almost evident when one uses the simple model [96], initially proposed to describe the atomic states on the surface.

For example, it is evident that when the nucleus is placed on the impenetrable plane, the 2p-orbital oriented in the direction of its normal defines the ground state. Indeed, this function is the solution of the Schrödinger equation that satisfies the Dirichlet boundary conditions in the half-space and has no nodal surfaces (except for the Dirichlet boundary). Similar considerations are very useful for the purpose of qualitative analysis. One may consider approaches of this sort as a clever development of ideas of classical works [97, 98] in which the energy of systems with spatial restrictions was assessed using the known energy values of the states of a free system, the wave functions of which have nodes in the right places. For more complex situations, but for the ground state only, one may use the simple geometric method proposed in [99] on the basis of some of comparison theorems [100].

In principle, for the study of the nuclear shift effects in degenerated states of atomic systems in a cavity, it would be natural to use the Jahn-Teller theorem (on its proof and some connected problems see also [101, 102]). Obviously, for the atomic system in the cavity of a fixed form, there are not more than three nuclear displacements that could be Jahn-Teller active in a conventional sense, while there exist a lot of asymmetrical cavity deformations that would play a similar role here.

2.7 Conclusion

In the present work, we have considered the simplest effect of symmetry reduction, namely, the splitting of degenerate energy levels of some model systems like the hydrogen atom or the isotropic harmonic oscillator under transition from a free system to a system in the cavity. Special attention was paid to the cavities of a large size. In some cases, the asymptotic analysis of the splitting was proposed. It was demonstrated that the observed energy level ordering in cavities results from interplay of numerous factors and the relative positions of the energy levels could change significantly with variations of the cavity shape within the fixed point symmetry group.

The problems discussed here are closely related to those often encountered within the Crystal Field Theory. However, the laws of the energy levels splitting are determined by similar but slightly different relations. For example, relations like Eq. (2.9) or (2.28) for cavities of a large size are reminiscent of the formulas of the Crystal Field Theory. But to study the splitting of levels of an atom in a polyhedral cavity, one should consider not the positions of the polyhedron vertices, but the positions of the touch points for the faces and the inscribed sphere. For regular polyhedra, these points specify the location of the vertices of the *dual polyhedron*. This circumstance itself leads to some peculiarities of the problem when one tries to compare the state ordering for atoms in polyhedral cavities and for the same atoms surrounded by systems of point charges.

Another important detail is a need for analysis of a number of sets of degenerate states with a given angular momentum in some cases and quasi-degenerated groups of states. In the case of cubic or octahedral systems, it has no essential influence on

the structure of the energy levels. For tetrahedral cavities, on the contrary, this is an additional complication, leading to inversion of the state ordering in some cases.

Obviously, a more consistent consideration of the effects of spatial restrictions on the motion of particles, taking into account all degrees of the freedom of the system and estimating, e.g. the transition probabilities, is desirable. As an example, the fully-dimensional quantum-mechanical problem of a hydrogen atom in a spherical cavity, studied numerically in [50], has been already mentioned. Implementation of the same ideas for more complicated cavities (and, perhaps, for more realistic models for the environment) requires, even in one-electron case, further development of more powerful and efficient tools for the analysis of the boundary value problems for the molecular Schrödinger equation.

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