A universal effective quantum number for centrally symmetric problems

2009 J. Phys. A: Math. Theor. 42 345202

(http://iopscience.iop.org/1751-8121/42/34/345202)

IOP PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **42** (2009) 345202 (15pp) doi:10.1088/1751-8113/42/34/345202

A universal effective quantum number for centrally symmetric problems

A A Lobashev and N N Trunov

D I Mendeleyev Institute for Metrology, 19 Moskovsky pr., St Petersburg 190005, Russia

E-mail: lobashev@vniim.ru and trunov@vniim.ru

Received 5 March 2009, in final form 3 July 2009
Published 6 August 2009
Online at stacks.iop.org/JPhysA/42/345202

Abstract

An effective quantum number that determines with high accuracy the level ordering in arbitrary centrally symmetric potentials for any space dimensionality is introduced and calculated by means of certain universal methods based on the known estimates for the total number of bound states in the same potential for various dimensionalities. Our new approach reproduces many known exact results. The effective number is used for constructing the periodic system of the atomic electron shells.

PACS numbers: 03.65.−w, 03.65.Sq, 03.65.Ge, 02.30.Mv

1. Introduction

The lack of analytic solutions for the most centrally symmetric potentials calls for the development of a method to approximate the spectra. Such a method is currently especially useful since besides known problems in atomic physics, theoretical models of nuclei [1] or quarkonium [2–4] there has recently arisen a number of new objects (metallic clusters [5, 6], etc) for which some analogies of the periodic system of shells may be constructed [7–9]. They may differ not only by the nature of the self-consistent field but also by their dimensionality d. A lot of effort has been made to obtain rigorous results (see e.g. [2–4, 10–12]), but these analogies only give some inequalities for special forms of potentials and only for $d = 3$.

A standard assumption is that the energy values depend on some linear combinations of the radial n_r and orbital l quantum numbers, i.e. $E(n_r, l) = E(\alpha n_r + \beta l)$. The Madelung–Kletchkovsky rule predicts the appearance of new shells (n_r, l) in the periodic system of the elements with increasing $n_r + 2l$ [7–9]. $E = E(3n_r + l)$ is expected for the metallic clusters [5, 6]; a similar quantum number for nuclei was proposed in [1] by using a certain classical analogy.

However, such a dependence of the exact spectra on some linear combinations is known only for the Coulomb and oscillator potentials:

$$V_c(r) = -\frac{Z}{r}, \quad E_c(n_r, l) = -C_c\,(\nu + \lambda)^{-2}\,, \tag{1}$$

$$V_{\rm osc}(r) = br^2, \quad E_{\rm osc}(n_r, l) = C_{\rm osc}\,(\nu + \lambda/2)\,, \tag{2}$$

$$\nu = n_r + \frac{1}{2}, \qquad \lambda(d) = l + \frac{d-2}{2}. \tag{3}$$

Two remarkable facts are known (at least for $d = 3$) for our reference potentials (1) and (2) and only for them. First, the usual WKB condition

$$\frac{1}{\pi}\int \sqrt{2\,(E - V(r)) - \frac{\lambda^2}{r^2}}\ {\rm dr} = \nu \tag{4}$$

leads to the exact spectra (1) and (2). For $d = 3$, the term λ^2/r^2 is known as the centrifugal potential with the Langer correction $l(l+1) \to (l+1/2)^2$ [13]. Second, for the oscillator, we have

$$\frac{1}{\pi}\int \sqrt{2\,(E - V(r)) - \frac{\lambda^2}{r^2}}\ {\rm dr} = \frac{1}{\pi}\int \sqrt{2\,(E - V(r))}\ {\rm dr} - \frac{\lambda}{2}. \tag{5}$$

In all cases, the integration limits are the corresponding turning points and we put $m = \hbar = 1$. Combining (4) and (5), we obtain

$$\frac{1}{\pi}\int \sqrt{2\,(E - V(r))}\ {\rm dr} = \nu + \frac{\lambda}{2}, \tag{6}$$

so that on the right-hand side of (6) we see the same linear combination of ν and λ as in (2).

In the present paper we generalize (6) and get an effective quantum number

$$T\,(n_r, l) \equiv \nu + \phi\lambda = \left(n_r + \frac{1}{2}\right) + \phi\left(l + \frac{d-2}{2}\right) \tag{7}$$

for any centrally symmetric potentials and any dimensionality of the problem by means of some generalization and new universal variations of the methods used earlier [14–16] in order to obtain T for $d = 3$. The coefficient ϕ is determined as a definite combination of the functionals $N_d[E; V]$, which represent asymptotic estimates for the total number of bound states in a given potential $V(r)$ with energies not exceeding E [17].

This quantum number T (7) determines the order of the bound states: $E(T) > E(T')$ if $T > T'$. For our reference cases (1) and (2), T coincides with $\nu + \lambda$ and $\nu + \lambda/2$ respectively. In a general case, T very well describes the real situation, but it is formally not the exact quantum number. Note that the principal quantum number $n = n_r + l + 1$ determines the spectrum only for the Coulomb potential and only if $d = 3$.

Hereafter, we present both our general method and several of its applications such as level ordering, screened Coulomb potentials, atomic shells ordering, etc. The general logical basis of our treatment is summarized in section 10.

2. The Schrödinger equation and its conformal transformation

We use the Schrödinger equation in the form ($m = \hbar = 1$)

$$\Delta_d\Phi + P^2\Phi = \left(\frac{\partial^2}{\partial r^2} + \frac{d-1}{r}\frac{\partial}{\partial r}\right)\Phi + \frac{\Delta_{d-1}(\Omega)\Phi}{r^2} + P^2\Phi = 0,$$
$$P^2 = 2\,(E - V(r))\,, \tag{8}$$

where $\Delta_{d-1}(\Omega)$ denotes the Laplace operator on the unit sphere S^{d-1}, E is the energy value and $V(r)$ is the potential. Equation (8) corresponds to the following metric:

$$ds^2 = dr^2 + r^2 d\Omega_{d-1}^2 \tag{9}$$

with $0 \leqslant r < \infty$ and Ω_{d-1} being coordinates on S^{d-1}.

In order to eliminate the first derivative in (8) and the singularity at $r = 0$, we represent the Schrödinger equation in a conformal metric $d\tilde{s}^2$ with a new variable $\rho = \ln r$ so that

$$ds^2 = r^2 d\tilde{s}^2 = e^{2\rho}\left(d\rho^2 + d\Omega_{d-1}^2\right).$$

With reference to [18], we obtain the following equation instead of (8):

$$\frac{d^2\Psi}{d\rho^2} + \Delta_{d-1}(\Omega)\Psi + K(d)\Psi + e^{2\rho}P^2\Psi = 0, \tag{10}$$

$$K(d) = -(d-2)^2/4, \qquad \Psi = \exp\left(\frac{d-2}{2}\rho\right)\Phi, \qquad -\infty < \rho < \infty. \tag{11}$$

We can prove (10) by a simple substitution of (11) into (8); for $d = 3$, this is the Langer transformation introduced earlier as an ad hoc form.

Taking into account the eigenvalues [19]

$$\Delta_{d-1}(\Omega)Y = -L^2 Y, \qquad L^2 = l(l+d-2), l = 0, 1, 2, \ldots, \tag{12}$$

and the term $K(d)$ in (11), for $\Psi = \psi(\rho)Y(\Omega)$ we obtain

$$\psi'' + W\psi - \lambda^2\psi = 0, \qquad \lambda = l + \frac{d-2}{2}, \tag{13}$$

$$W(E, \rho) = r^2 P^2(r) = 2e^{2\rho}\left(E - V(e^{\rho})\right). \tag{14}$$

The usual condition $\Phi(r = 0) < \infty$ leads to $\psi(\rho) \to 0$ if $\rho \to -\infty$. The exact spectra of (8) and (10), (13) must be identical as Φ and Ψ are only distinguished by a positive factor $e^{2\rho}$.

We have seen that the usual 'automatic' replacement $l(l+1) \to \lambda^2$ actually means that we work in a new special conformal curved space; its curvature is $Ke^{-2\rho}$ with K from (11). Instead of the topology $R^d = S^{d-1} \times (0, \infty)$, we get $S^{d-1} \times (-\infty, \infty)$ in the conformal space. Coordinates (ρ, Ω) are similar to the Cartesian ones in the maximum possible measure: ρ is a harmonic coordinate, a field of the parallel vectors exists and all sections $\rho = \text{const}$ are identical [20]. That is why the leading WKB approximation in the conformal space gives the best possible result (while exact spectra must be identical in the two metrics ds^2 and $d\tilde{s}^2$).

Some refined calculations [19] show that the number of eigenstates for equation (12) is

$$D(l) = \frac{(l+d-1)!}{l!(d-1)!} - \frac{(l+d-3)!}{(l-2)!(d-1)!}$$

or after some arithmetic

$$D(l) = \frac{2S(l)}{(d-2)!}\left(l + \frac{d-2}{2}\right), \tag{15}$$
$$S(l) = (l+d-3)(l+d-4)\ldots(l+2)(l+1).$$

$S(l)$ contains $(d-3)$ factors, so that the two leading terms in l are

$$D(l) = \frac{2l^{d-2}}{(d-2)!} + \text{const} \cdot l^{d-3}.$$

Now let us express $D(l)$ through λ (13). By multiplying the first and the last factors of S (15), then multiplying the second and the last but one factors and so on, we obtain

$$S = \left[\lambda^2 - \left(\frac{d}{2} - 2\right)^2\right]\left[\lambda^2 - \left(\frac{d}{2} - 3\right)^2\right]\ldots$$

where the last factor is $(\lambda^2 - 1/4)$ if $d - 3$ is even or simply λ if $d - 3$ is odd. In any case, the leading terms are

$$D(\lambda) = \tilde{D}(\lambda) + \text{const} \cdot \lambda^{d-4}, \qquad \tilde{D}(\lambda) = \frac{2\lambda^{d-2}}{(d-2)!}. \tag{16}$$

Thus, $D(\lambda)$ has no term of order λ^{d-3} unlike $D(l)$. That is why λ is the most suitable variable with the smallest distinction between D and the leading term $\tilde{D}$.

The WKB quantization condition for (13) is

$$I(E, \lambda) \equiv \frac{1}{\pi}\int \sqrt{W(E, \rho) - \lambda^2}\, \mathrm{d}\rho = n_r + \frac{1}{2} \equiv \nu. \tag{17}$$

We find (17) to be identical to (4) when we return to the previous variables r and P^2 (8).

3. Linear approximation of the WKB integral

As we have already seen, $I(E, \lambda)$ is linear in λ for the oscillator and Coulomb potentials. In the general case, we can write

$$N_1(E) \equiv I(E, 0) = I(E, \lambda) + \phi\lambda + q(E, \lambda), \tag{18}$$

where q denotes all nonlinear corrections. For the above cases (1) and (2), $q \equiv 0$ and $\phi = 1, \phi = 1/2$ respectively. For determining ϕ, we use hereafter the known estimates N_d for the total number of bound states in a d-dimensional problem with the energies not exceeding E [17]; being expressed in our variables W, ρ, they are

$$N_d = \frac{B\left(\frac{3}{2}, \frac{d-1}{2}\right)}{\pi(d-2)!} M_d(E), \qquad M_d(E) = \int W^{d/2}(E, \rho)\, \mathrm{d}\rho, \quad d \geqslant 2, \tag{19}$$

where $B(y, z)$ is the beta function. We will show how to obtain N_d (19) using (17) and (16). At a fixed λ (5), equation (17) determines energies of the bound states. It is evident that the maximum value of ν corresponds to the maximum energy so that $I(E, \lambda)$ is equal to the total number of bound states with a given λ and values of energies not exceeding E (similar to that in WKB, we neglect the difference between n_r and ν in this case too). Now we have to take into account the degeneracy of states (16). Using the universal form of the first term $\tilde{D}$, we multiply $I(E, \lambda)$ (17) by $\tilde{D}$ and integrate with respect to λ over the domain $0 \leqslant \lambda \leqslant A$:

$$A^2(E) = \max_{\rho} W(E, \rho).$$

We suppose that $W(E, \rho)$ has a sole maximum at any E. In intermediate calculations, we treat λ as a continuous variable. Changing the order of integration, we obtain

$$\int_0^{A(E)} \tilde{D}(\lambda) I(E, \lambda)\, \mathrm{d}\lambda = N_d(E) \tag{20}$$

with N_d from (19). Thus, the leading term $\tilde{D}$ instead of D must be used in WKB methods.

Now we return to (18) and intend to choose the value of ϕ so that $q(E, \lambda)$ averaged over all bound states becomes zero. Multiplying both sides of (18) by $\tilde{D}$ and integrating with respect to λ, we obtain

$$\frac{N_d}{A^d} = \frac{2N_1}{A(d-1)!} - \frac{2\phi}{d(d-2)!}. \tag{21}$$

As N_d is proportional to A^d, the value of ϕ does not depend on A. It is also invariant under the transformation $r \to ar$, i.e. $\rho \to \rho + \ln a, a > 0$. In order to simplify (21), we introduce relative parameters χ_d comparing N_d for a given potential with $N_d^{(c)}$ for the above reference case: the Coulomb potential with the same value of A as in N_d. We have $A^2 = Z^2/2|E|$ for W (14) with $V = -Z\exp(-\rho)$. Calculating N_d (19), we get at any Z and $E < 0$

$$\chi_d = \frac{N_d}{N_d^{(c)}} = \frac{d!N_d}{2A^d}, \qquad d \geqslant 2, \qquad \chi_1 = \frac{N_1}{A}. \tag{22}$$

Substituting (22) into (21) and using (19), we finally obtain

$$\phi = \chi_1 + \frac{\chi_1 - \chi_d}{d-1}, \qquad \chi_d = \frac{M_d}{A^d m_d}, \qquad m_d = B\left(d/2, 1/2\right). \tag{23}$$

In the general case, we have $\phi = \phi(d, E)$. For our reference cases (1) and (2), $\phi = \chi_d = \text{const}$ does not depend on d or on E and coincides with $\phi = 1, 1/2$. Thus, we have obtained the desired effective quantum number T (7) with ϕ of (23). All the parameters χ_d, ϕ are some functionals of a given potential, such as $\phi = \phi[V]$, etc, as well as some functions of E and d.

The quantization condition (17) with respect to (18) and (21) takes the following form:

$$A(E)\chi_1(E) = \frac{1}{\pi}\int \sqrt{2\left(E - V(r)\right)}\,\mathrm{dr} = T\left(n_r, l; \phi(E)\right). \tag{24}$$

The functions $\chi_d(E)$ may be treated as a special nonlinear transform of a given potential $V(r)$. This transformation is the most adequate one for our method. Note that ϕ and χ_d are invariant under the transformation $W \to BW$ with $B > 0$.

In what follows, we will treat (23) as the basic form for ϕ. Nevertheless, it is useful to find another approximation for ϕ and to compare them in order to evaluate their accuracy. Suppose that we construct a multiplicative expression for ϕ:

$$\phi_m(E, d) = C N_d^{\alpha} N_1^{\beta}$$

using only integral estimates N_d and excluding the above parameter A. Since $N_d \propto A^d$, we must put $\alpha d + \beta = 0$. Substituting χ_d instead of N_d, we get $\phi_m = C'\left(\chi_1 \chi_d^{-1/d}\right)^{\beta}$. Requiring that $\phi_m = \chi_d = \phi$ for our reference cases, we finally have

$$\phi_m(E, d) = \left(\frac{\chi_1^d}{\chi_d}\right)^{\frac{1}{d-1}}. \tag{25}$$

The same value of ϕ_m was obtained earlier using a duality between certain pairs of power-law potentials [15]. As we will see, χ_d is a smooth monotonic function of d for all interesting model potentials. We introduce a convenient auxiliary function f_d:

$$\chi_d = \chi_\infty \exp(f_d); \tag{26}$$

then the ratio of ϕ_m to ϕ is

$$R = \frac{\phi_m}{\phi} = 1 + \frac{d}{2(d-1)^2}\left(f_1 - f_d\right)^2 + \mathrm{O}(f^3). \tag{27}$$

Numerical calculations show that R is very close to 1, so that $R - 1 < 0.01$ and in most cases < 0.002 in a wide interval of E for a wide set of potentials studied and for all d (see table 1). This proximity of two values of ϕ calculated by quite different methods confirms the objective character of ϕ and of the effective quantum number T itself. We shall return to this proximity in section 7.

Note that we may treat d in M_d, χ_d and so on as a continuous variable in intermediate calculations.

Table 1. Values of χ_d and ϕ for several potentials: (41*a*)–(41*d*) and (28), as well as $\phi_m(3)$ (25).

	$V(r)$	χ_∞	χ_3	χ_2	$\chi_1 = \phi(\infty)$	$\phi(3)$	$\phi(2)$	$\phi_m(3)$
$E = 0$	(41*a*)	1.414	1.376	1.359	1.316	1.286	1.273	1.286
	(41*b*)	2	2	2	2	2	2	2
	(41*c*)	1.826	1.803	1.793	1.769	1.752	1.745	1.752
	(41*d*)	1.89	1.87	1.84	1.78	1.74	1.72	1.75
$E \to -\infty$	(41*a*)–(41*d*)	1	1	1	1	1	1	1
	$\mu = -1$	1	1	1	1	1	1	1
	$\mu \to 0$	0.707	0.688	0.680	0.658	0.644	0.636	0.643
$V = br^\mu$	$\mu = 1$	0.577	0.568	0.563	0.551	0.543	0.539	0.544
	$\mu = 2$	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Any E	$\mu = 3$	0.447	0.457	0.461	0.469	0.475	0.477	0.476
	$\mu \to \infty$	0	0.212	0.250	0.318	0.371	0.386	0.390

4. Nonlinear transform χ_d for the power-law potentials

In this section, we will study power-law potentials

$$V(r) = br^\mu, \qquad b\mu > 0 \tag{28}$$

with $-2 < \mu < \infty$. For them, the functions χ_d (22) and ϕ (23) are monotonic and do not depend on E:

$$\chi_d(\mu) = \left(\frac{2+\mu}{2}\right)^{\frac{2+\mu}{2}\frac{d}{\mu}} \frac{2^{d/2}}{\mu^{d/2+1}} \frac{B(d/\mu, d/2+1)}{B(d/2, 1/2)} \qquad (\mu > 0),$$
$$\chi_d(\mu) = \left(\frac{2}{2-|\mu|}\right)^{\frac{2-|\mu|}{2}\frac{d}{|\mu|}} \frac{2^{d/2}}{|\mu|^{d/2+1}} \frac{B\left(d\frac{2-|\mu|}{2|\mu|}, \frac{d}{2}+1\right)}{B(d/2, 1/2)} \qquad (-2 < \mu < 0). \tag{29}$$

In the limiting case $d \to \infty$, we obtain from (28) and (29), for all $\mu > -2$,

$$\chi_\infty = \frac{1}{\sqrt{\mu+2}}. \tag{30}$$

It is quite natural that expression (29) does not depend on d if $\mu = 2$, $\mu = -1$. Values of χ_d and ϕ (23) are shown in table 1.

For the power-law potentials, the following expansion f_d (26) with χ_∞ (30) is valid:

$$f_d = \sum_{k=1}^{\infty} \frac{b_k}{d^k}, \qquad \chi_d = \chi_\infty \left(1 + \frac{b_1}{d} + \cdots\right) \tag{31}$$

$$b_1(\mu) = \frac{(\mu+4)^2}{12(\mu+2)} - \frac{3}{4}, \qquad b_3(\mu) = \frac{1}{360}\left(7 + \frac{8\mu^3}{(\mu+2)^2}\right), \qquad b_2 = b_4 \equiv 0. \tag{32}$$

The values of both b_1 and b_3 are equal to zero for the oscillator and Coulomb potentials, and are small in the vicinity of $|b_3| \ll |b_1|$ and $b_1 b_3 < 0$. Correspondingly, the ratio R (27) is very close to 1. At any fixed d, the value of $\phi(d, \mu)$ (23) with χ_d (29) decreases monotonically with increasing μ.

All model potentials checked by us reveal similar simple asymptotical behavior. It seems to be a typical peculiarity of any physically reasonable potential. That is why our method may be universal enough (not including artificial counterexamples).

5. The level ordering in accordance with T and exact results

Since the level ordering is a very important property of many-particle systems, many authors have tried to obtain exact theorems for several special forms of potentials and for $d = 3$. Our effective quantum number T (7) together with condition (24) immediately leads to the universal behavior for all potentials $V(r)$:

$$\mathrm{sgn}\big(E(T) - E(T')\big) = \mathrm{sgn}\left(T - T'\right), \tag{33}$$

since the left-hand side of condition (24) is a monotonic function of E. In this section, we show that our expressions (7) and (23) for T are exact enough to reproduce many known or expected results.

It is interesting to compare expression (33) with known results. The first example connects two differential operators ($d = 3$)

$$\begin{aligned} Y_1[V] &= r\frac{\mathrm{d}^2}{\mathrm{d}r^2}(rV) = r\frac{\mathrm{d}V}{\mathrm{d}r}\left(\kappa(r)+1\right), \\ Y_2[V] &= \frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}V}{\mathrm{d}r}\right) = \frac{1}{r^2}\frac{\mathrm{d}V}{\mathrm{d}r}\left(\kappa(r)-2\right), \\ \kappa(r) &= 1 + \frac{r\left(\mathrm{d}^2V/\mathrm{d}r^2\right)}{\mathrm{d}V/\mathrm{d}r} \end{aligned} \tag{34}$$

with two energy differences respectively:

$$\begin{aligned} D_1 &= E(n_r+1, l) - E(n_r, l+1), \\ D_2 &= E(n_r, l) - E(n_r-1, l+2). \end{aligned} \tag{35}$$

We have introduced an auxiliary function $\kappa(r)$; for power-law potentials $\kappa(r) \equiv \mu$.

The theorem proved in [10, 12] states in our notation that

$$\mathrm{sgn}Y_1 = \mathrm{sgn}D_1, \qquad \mathrm{sgn}Y_2 = \mathrm{sgn}D_2 \tag{36}$$

if $\mathrm{sgn}Y_k = \mathrm{const}$ for $0 < r < \infty$. Suppose that our T method is exact. Then, since for monotonic attractive potentials $\mathrm{d}V/\mathrm{d}r > 0$ in (34), using (33), we can write instead of (36)

$$\begin{aligned} \mathrm{sgn}Y_1[V] &= \mathrm{sgn}\left(\kappa(r)+1\right) = \mathrm{sgn}\left(T(n_r+1, l) - T(n_r, l+1)\right), \\ \mathrm{sgn}Y_2[V] &= \mathrm{sgn}\left(\kappa(r)-2\right) = \mathrm{sgn}\left(T(n_r, l) - T(n_r-1, l+2)\right). \end{aligned} \tag{37}$$

For power-law potentials, we have $\phi = \phi[\mu]$ which does not depend on E and $\kappa = \mu$. Substituting T (7) into (37), we get two equations equivalent to (36):

$$\mathrm{sgn}\left(\mu+1\right) = \mathrm{sgn}(1-\phi), \tag{38a}$$

$$\mathrm{sgn}\left(\mu-2\right) = \mathrm{sgn}(1-2\phi). \tag{38b}$$

Equality (38a) occurs for all potentials (28) since ϕ (23) with χ_d (29) is a monotonic function of μ (see the examples in table 1): $\phi = 1/2$ for $\kappa = \mu = 2$ and $\phi = 1$ for $\kappa = \mu = -1$.

Another exact statement is as follows [4]: for power-law potentials (28) $\mathrm{d}^2E(0, l)/\mathrm{d}l^2 > 0$ if $\mu > 2$. From our condition (24), we immediately obtain

$$E(n_r, l) = C_\mu T^{\frac{2\mu}{\mu+2}} = C_\mu\left(\nu + \phi\lambda\right)^{\frac{2\mu}{\mu+2}}, \quad C_\mu > 0, \mu > 0,$$

$$\mathrm{sgn}\frac{\partial^2 E}{\partial l^2} = \mathrm{sgn}(\mu-2),$$

so that the above-mentioned inequality is valid for our T.

We will also study a family of potentials for quarkonium systems [4] in section 9.

6. Screened Coulomb potentials

In this section, we will study with the help of our new method another actual and interesting class of centrally symmetric potentials:

$$V(r) = -\frac{Zg(r)}{r}, \qquad g(0) = 1, \qquad g > 0, \qquad \frac{\mathrm{d}g}{\mathrm{d}r} < 0. \tag{39}$$

The Thomas–Fermi potential $V_{\mathrm{TF}}(r)$ of the self-consistent field in the many-electron atoms [21] also belongs to type (39). All such model atomic potentials must obey the inequality $g'' > 0$. It follows from the Poisson equation

$$\Delta U = \frac{Y_1[U]}{r^2} = -4\pi\rho$$

for the electrostatic potential U, so that $V = -|e|U$ and the electron charge density $\rho < 0$. $\mathrm{sgn}Y_1[V] = -\mathrm{sgn}Y_1[U] = -1$; correspondingly, we get from (34) $\kappa < -1$. At the same time, for (39) we obtain

$$\kappa = -1 + \frac{g''r^2}{g'r - g} = -1 - \frac{g''r^2}{|g'r| + |g|} \tag{40}$$

with respect to inequalities (39), so that $g'' > 0$. There are also important potentials with

$$g(r) = \mathrm{e}^{-r}, \tag{41a}$$

$$g(r) = \frac{1}{(1+r)^2}, \tag{41b}$$

$$g(r) = \frac{1}{(1+r)^{2.5}} \tag{41c}$$

besides

$$V_{\mathrm{TF}}(r). \tag{41d}$$

For all these potentials, the values χ_d and $\phi(d)$ depend on the value of the energy E. For the deepest levels only a small domain $r < r_t \to 0$ is classically accessible in (24) ($V(r_t) = E$), so that we have $\kappa \to -1$ and $\chi_d \to \phi(d) \to 1$. In our quantum problem the deepest level has small $r_t \neq 0$ as well as $E \neq -\infty$, so formally there is a very small distinction from this limiting value of $\chi_d, \phi(d)$.

In the opposite extreme case $E \to -0$, corresponding values of χ_d and $\phi(d)$ for (41*a*)–(41*d*) are shown in table 1. These values asymptotically coincide in the depth of the potential well where there is no screening and the turning point $r_t \to 0$ for these $V(r)$. In table 1 we have placed χ_d and $\phi(d)$ for some power-law potentials (28), including $\mu \to \infty$ (the rectangular potential well) as well as multiplicative $\phi_m(3)$ from (25).

Let us demonstrate two ways of using T (7) taking as an example the model potential (41*c*) which is a very good approximation of the real self-consistent atomic potential [22] with Z being the nuclear charge. If we fix $E = 0$, then (24) indicates the order in which new bound states appear with increasing Z as well as corresponding values of Z. In contrast, at $Z = \mathrm{const}$ we get the level succession of all the bound states in a given atom with a fixed Z. It can be easily seen from table 1 and (24) that shallow levels ($E \approx 0$) are governed by $n_r + 1.75l$ ($d = 3$) but the deepest levels by $n_r + l$ (i.e. they are Coulomb-like ones), with intermediate behavior for middle levels. The introduced T ordering formalizes the well-known quantitative picture and in particular explains the periodic system of the elements; see the following section.

Our method is valid and simple not only for potentials with a non-trivial analytic form as (41*c*) but also for potentials given numerically. So for the Thomas–Fermi atomic potential, we obtain $\phi(3)$ which is very close to the corresponding value of (41*c*).

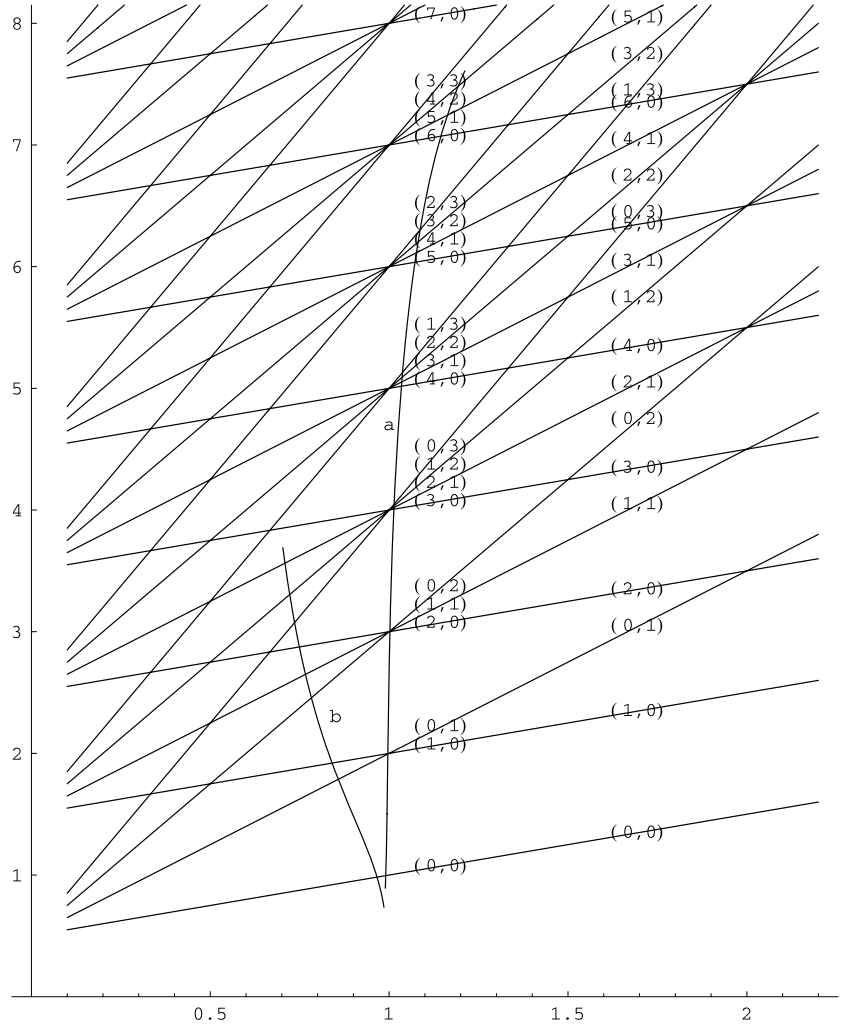

Figure 1. The effective quantum number T (7) versus ϕ (23) for the bound states (n_r, l) with n_r and l being the radial and orbital quantum numbers respectively. Lines with $l > 3$ are omitted for the sake of simplicity. Curves for the Yukawa potential $V(r) = -50\mathrm{e}^{-r}/r$ (a) and the quarkonium potential $V(r) = 3\,(-1/r + r)$ (b).

7. Universal diagram

The regular filling of shells in a centrally symmetric system with an arbitrary dimensionality and nature of the self-consistent field is clearly described in figure 1. In this figure, each line represents $T(n_r, l, \phi)$ as the linear function of ϕ at fixed (n_r, l). The crossing of two lines marks the values of ϕ which change the order of the level succession. Two different types of problems may be treated with the help of this diagram.

If $E = 0$, the value of ϕ is invariant under the transformations $V \to cV, r \to c_1 r$; this value does not depend on Z (even if $g = g\,(rf(Z))$. However, this is not the case if $E \neq 0$. With increasing strength of the potential (i.e. Z in (39)) new shells (n_r, l) with $E = 0$ appear

in the order of increasing $T(n_r, l)$ at a given value of $\phi(E = 0)$, i.e. along the vertical line $\phi = \text{const}$. Each shell can contain $D(l, d)$ (15) states; only this number D depends on d. When the shell (n_r, l) is filled in, i.e. all states are occupied with particles, the filling of the next shell (n_r', l') begins with the value $T' > T$ nearest to T.

It is known that the structure of the periodic system of the elements corresponds to the definite order of the filling of the atomic shells with increasing Z [7, 22]. The actual order of the shells is well known: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, i.e. (0, 0), (1, 0), (0, 1), etc. It takes place if and only if

$$5/3 < \phi(3) < 2 \tag{42}$$

as follows from figure 1; for the first time, this range was found in another equivalent form of the atomic potential asymptotics [14, 22]. The most probable value $\phi \approx 1.75$ corresponds to the Thomas–Fermi potential as well as to (41*c*) and satisfies (42).

The usual supposed shells' ordering in metallic clusters [6] means that $\phi = 1/3$ in our notation. We have obtained the close value $\phi(3) \approx 0.37$ for all levels in the rectangular potential well (28) with $\mu \to \infty$. As can be seen from figure 1, the T ordering exactly reproduces the level ordering calculated for (28) with $d = 3$ and several values of μ, e.g. for $\mu = 0.1, \phi \approx 0.63$ [11] and $\mu \to \infty, \phi \approx 0.37$.

Another situation arises if we treat $\phi(E)$ and the left side of condition (24) $A(E)\chi_1(E)$ at a fixed E as a point $(\phi(E), A(E)\chi_1(E))$ on the plane of the diagram. By changing E we obtain a curve, the form of which depends on a given potential $V(r)$.

At an arbitrary point, we cannot find the integer (n_r, l) satisfying (24). Such an integer (n_r, l) only exists for these points where one of the lines $T(n_r, l, \phi)$ crosses the curve. Thus, these distinguished points indicate the actual bound states and indirectly their energies. The curve clearly shows how the level ordering changes with changing E or T (remember that $\mathrm{d}T/\mathrm{d}E > 0$). As an example, we show such curves for the Yukawa potential $V(r) = -50\mathrm{e}^{-r}/r$ in figure 1(*a*) and for the quarkonium potential $V(r) = 3\,(-1/r + r)$ in figure 1(*b*).

8. Asymptotic behavior of χ_p and ϕ and a nonlinear quantization condition

As we have demonstrated in the previous sections, our method with the approximation of linearity in λ for T is sufficiently exact. Meanwhile, we can take into account nonlinear corrections. In this section, we will introduce a nonlinear expression for our effective quantum number T and demonstrate its new possibilities. Let us use the fact that the integral (19) has the original form for the asymptotic Laplace expansion:

$$M_d = \int W^{d/2}(x)\,\mathrm{d}x \approx A^{d+1}\sqrt{\frac{4\pi}{|W^{(2)}|d}}\left(1 + \frac{a_1}{d} + \frac{a_2}{d^2} + \cdots\right), \tag{43}$$

where a_k are known functions of the derivatives $W^{(n)}$ taken at the maximum point $r = r_m, A^2 = W(r_m)$. Expanding m_d in the denominator of (23) similarly to (43) we obtain an asymptotic expansion of χ_d ((26) and (31)), where

$$\chi_\infty = A\sqrt{\frac{2}{|W^{(2)}|}}. \tag{44}$$

A special case of such an expansion is (32). Of course, we can also calculate χ_∞ as $\lim \chi_d$ for $d \to \infty$ (even for nonanalytic potentials, when (44) may be incorrect). One can easily prove numerically that all the interesting model potentials including those represented in table 1

have $b_1 \ll 1$, $|b_2| \ll |b_1|$ and so on. For example, for power-law potentials (28) we have $b_1(0) = -0.08$, $b_1(4) = 0.139$ according to (32), and only in an unreal case $\mu \approx 15$ do we get $b_1(\mu) \approx 1$. Thus, the asymptotic regime is already reached for $d \geqslant 1$ (actually for $d \geqslant 0.5$). That is why χ_d are smooth monotonic functions for $d \geqslant 1$.

Using $\kappa(r)$ (34), we can get an interesting expression equivalent to (44):

$$\chi_\infty = \sqrt{\frac{2}{\kappa(r_m) + 2}}. \tag{45}$$

For power-law potentials, $\kappa \equiv \mu$ and we return to (30).

Neglecting in f_d ((26) and (31)) all terms with $d \geqslant 2$, we obtain a simple approximation

$$\chi_d \approx \chi_d^{(as)} = \chi_\infty + \frac{\chi_1 - \chi_\infty}{d}. \tag{46}$$

Substituting (46) into (23), we also have

$$\phi(d) \approx \phi^{(as)}(d) = \chi_1 + \frac{\chi_1 - \chi_\infty}{d}. \tag{47}$$

Finally comparing (46) and (47), we obtain another approximate expression

$$\phi(d) \approx \chi_D^{(as)}, \qquad D = \frac{d}{d+1}. \tag{48}$$

We have calculated ratios $s = \phi^{(as)}(d)/\phi(d)$ and $\chi_D^{(as)}/\phi(d)$, where $\phi(d)$ is the basic form (23) for various potentials and for a wide interval of E. It turns out that even for $d = 3$ both s and w are close to unity: $|s - 1|, |w - 1| \leqslant 0.02$ and in most cases $\leqslant 0.01$.

As we have already said, the closest approximation to the basic additive form ϕ is the multiplicative form ϕ_m (25): for their ratio $R = \phi/\phi_m$ we have $R - 1 < 0.01$ and in most cases < 0.002 (see table 1). Each of these approximations may be preferable in some particular situations.

A simple universal form $\chi_d^{(as)}$ (46) allows us to get a universal nonlinear approximation

$$I(\lambda) = I(0) - F(\lambda) \tag{49}$$

for $I(E, \lambda)$ (17). Similar to what we have done in section 3, instead of (23) we obtain

$$\frac{d}{A^d} \int_0^A F(\lambda) \lambda^{d-2} \, \mathrm{d}\lambda = \frac{d\chi_1 - \chi_d}{d-1}. \tag{50}$$

If we assume $F = \phi\lambda$ in (50), we return to ϕ as in (23). But this time we will use χ_d (46) and thus come to a simple Melline transform for $F(\lambda)\lambda^{-1}$:

$$\frac{1}{A^d} \int_0^A F(\lambda) \lambda^{d-2} \, \mathrm{d}\lambda = \frac{\chi_1}{d} + \frac{\chi_1 - \chi_\infty}{d^2}, \qquad F(\lambda) = \chi_1 \lambda + (\chi_1 - \chi_\infty)\, \lambda \ln(\lambda/A). \tag{51}$$

Correspondingly, we obtain a nonlinear quantization condition

$$A(E)\chi_1(E) = T_{\mathrm{non}}(n_r, l), \qquad T_{\mathrm{non}}(n_r, l) = \nu + F(\lambda). \tag{52}$$

Both (51) and (52) become incorrect if $\lambda/A \ll 1$, but actually if $d \geqslant 3$ we have $\lambda \neq 0$ and a finite λ/A even for $l = 0$ (see (13)); in real systems usually $A \approx \lambda_{\max} \leqslant 5$.

Let us reproduce a delicate distinction obtained for the power-law potentials (28) by means of the $\hbar$-expansion of the Regge trajectories [23]. Using our notation, we can rewrite the final result [23] in a simple form for $\mu > -1$:

$$\mathrm{sgn}\,(E^\sigma(0, l+1) - 2E^\sigma(0, l) + E^\sigma(0, l-1)) = \mathrm{sgn}(2 - \mu), \qquad \sigma = \frac{2\mu}{\mu + 1}. \tag{53}$$

Since $E \propto T^{\frac{1}{\sigma}}$ for (28), the left-hand side of (53) is linear in T; by substituting T_{non} (52) in (53), we obtain

$$\operatorname{sgn}(\chi_\infty - \chi_1) \cdot \operatorname{sgn}\Lambda = \operatorname{sgn}(\chi_\infty - \chi_1) = \operatorname{sgn}(2-\mu), \tag{54}$$
$$\Lambda = (\lambda+1)\ln(\lambda+1) + (\lambda-1)\ln(\lambda-1) - 2\lambda\ln\lambda.$$

We have used here the fact that $\mathrm{d}^2(x\ln x)/\mathrm{d}x^2 > 0$, so that $\Lambda > 0, \operatorname{sgn}\Lambda = 1$. But the last equality (54) is valid for our χ_d; see table 1. It should be stressed that in any linear approximation the left-hand side of equation (53) is equal to 0 and not to 1 as for Λ, so that only nonlinear approximation confirms the strong result [23].

9. The level ordering for quarkonium systems

In this section, we will study the family of potentials for quarkonium systems [4]:

$$V_q(\alpha,\delta,r) = B\left(-\frac{\alpha}{r} + (1-\alpha)r^\delta\right), \qquad 0<\alpha<1, \quad \delta>0, \quad B>0. \tag{55}$$

The following ordering was assumed for V_q:

$$E(0,1) < E(1,0) < E(0,2). \tag{56}$$

For this family, we have $\partial V/\partial r > 0$, $\mathrm{d}k/\mathrm{d}r > 0$,

$$-1 < \kappa(r) = \frac{-1+Q\mu^2}{1+Q\mu} < \kappa(\infty) = \delta, \qquad Q(r) = \frac{1-\alpha}{\alpha} r^{\delta+1} \tag{57}$$

for any $r > 0$. Thus, equation (36) holds and predicts the ordering (56), but only for $\delta \leqslant 2$ (if $\delta > 2$, $\operatorname{sgn}(\kappa - 2)$ changes its sign when r is large).

Now we will study how our T method works in this situation. Since we act within the WKB frame, we will introduce a natural weak

Conjecture 1. *The level ordering satisfies (37) if* $\operatorname{sgn}(\kappa - 2) = \text{const}$ *in the classically accessible domain:*

$$r < r_t, \qquad V(r_t) = E \tag{58}$$

(we suppose $\partial V/\partial r > 0$ *for our potentials).*

This conjecture allows us to maintain the previous level ordering (as for $\mu \leqslant 2$) even when $\delta > 2$. It is easy to calculate that for (55) $\mathrm{d}\kappa(r_t)/\mathrm{d}\alpha < 0$, so that we can have $\kappa(r_t) < 2$ for small values of energy or for middle values of α but $\kappa(r_t) > 2$ and the inverse ordering $E(1,0) > E(0,2)$ if $B(1-\alpha)$ is great enough. Rigorous results [4] confirm these conclusions. Note that for $\alpha \ll 1$, the Coulomb term is negligible in (55) even for the deepest levels as compared with $B(1-\alpha)r^\delta$. It also seems reasonable to make a strong

Conjecture 2. *For any potential with a smooth* $\mathrm{d}\kappa/\mathrm{d}r$*, the value of* ϕ *can be well approximated as* $\phi[\mu]$ *for the power-law potential (28) with* $\mu = \kappa(r_m)$*. Here* r_m *depends both on the value of the energy and on the parameters of a given potential, and* r_m *is defined as* $W(r_m) = \max$.

This conjecture is exact for χ_∞; compare (30) and (45). Each χ_d and thus ϕ, as follows from (31) and (43), includes functions b_k depending on some derivatives $W^{(n)}(r_m)$. We can express $W^{(n)}(r_m)$, a_k (43) and correspondingly b_k (31) by means of $\kappa(r)$ (34). For example, the main terms take the following form:

$$\chi_d = \chi_\infty[\mu_m]\left(1 + \frac{b_1[\mu_m] + b_1^{\text{add}}}{d} + \cdots\right)$$

with $\mu_m \equiv \kappa(r_m)$, χ_∞ according to (30) or (45), $b_1[\mu]$ from (32), a new function $b_1^{\rm add}$ depending on $\kappa(r_m)$ in such a way that $b_1^{\rm add} \equiv 0$ if $\kappa(r) = \text{const}$ and

$$\frac{\mathrm{d}\kappa}{\mathrm{d}x} = r_m \frac{\mathrm{d}\kappa(r_m)}{\mathrm{d}r}.$$

Using (49), we can write for $d = 3$, with the same accuracy,

$$\phi = \phi(\mu_m) + \phi^{\rm add}, \qquad \phi^{\rm add} = \frac{4b_1^{\rm add}}{3\sqrt{\mu_m + 2}}$$

with one of the previous expressions for ϕ. In most or in fact in all of the real cases, we have $\phi^{\rm add} \ll \phi$. The first approximation, which neglects κ_r^2, κ_{rr} and is linear in λ is as follows

$$b_1^{\rm add} = \frac{16 + \kappa(r_m)}{24\,(\kappa(r_m) + 2)} r_m \frac{\mathrm{d}\kappa(r_m)}{\mathrm{d}r}.$$

Using (57), we get

$$\frac{\mathrm{d}\kappa}{\mathrm{d}x} = r\frac{\mathrm{d}\kappa}{\mathrm{d}r} \sim \frac{1}{Q(r_m)} \ll 1$$

at large Q. The condition $Q \gg 1$ is fulfilled at large E and/or large $B(1-\alpha)$. Thus, we obtain 'non-adiabatic' corrections $b_1^{\rm add} \ll b_1$, $\phi^{\rm add} \ll \phi$.

Then the coincidence of the two levels

$$T(0, 2) - T(1, 0) = 1 - 2\phi$$

is possible if $\delta > 2$ and E or $B(1-\alpha)$ are large enough. So the line $1 - 2\phi = 0$ on the plane $(\delta, B(1-\alpha))$ divides two domains with opposite level ordering. Note that $r_m < r_t$; for the above case

$$r_m \sim \left(\frac{2}{2+\delta}\right)^{\frac{1}{\delta}} r_t < r_t.$$

Note that both χ_d and ϕ are some smooth monotonic functions of E and d for all potentials in table 1.

10. Conclusion

Thus, we have constructed and calculated the effective quantum number T (7) which determines the appearance and ordering of the bound states in centrally symmetric potentials with very high accuracy. It should be stressed that different potentials may have very close or coinciding values of ϕ and T and hence identical level ordering (see e.g. cases (41*b*) and (41*c*) in table 1).

Although using the Thomas–Fermi potential for explaining the periodic system is partially successfully, it does not mean that this potential is the genuine or the best one. The point is that its value of ϕ is situated not too close to the limiting points of the interval (46) so that various corrections not taken into account in the Thomas–Fermi approach can only slightly change the value of ϕ within this interval. Hence, the level ordering is really the same as for the Thomas–Fermi potential.

The effective number T actually replaces the principal quantum number $n = n_r + l + 1$ for all potentials besides the Coulomb one with $d = 3$.

Using T, we immediately reproduce many results obtained for the level ordering by means of special theorems and numerical calculations. Moreover, the quantization condition (24) with T can also be used for determining the spectra. The accuracy of the energy values calculated for $V(r) = r$ is 0.3–0.5% and even in the worst case of the non-analytic potential well ($\mu \to \infty$) errors do not exceed 3–5% [16]. For two potentials with the same value of ϕ

we usually obtain different A and χ_1, so that the energies of their bound states do not coincide unlike the level ordering.

Let us summarize our main results. We have found step by step a special nonlinear transformation from a given $V(r)$ to a new function $\chi_d(E)$, where integer values of the new variable d coincide with the dimensionality. First of all, we have introduced nonlinear momenta $M_d(E)$ (19). Then we determine the 'strength' A of a given potential $V(r)$ as the maximum value of the classical angular momentum rP (see (14)). Finally, we compare a given $V(r)$ with our reference potential with the same value of A by means of $\chi_d(E)$ ((22) and (23)). They are smooth functions of E and do not depend on E for power-law potentials. As functions of d^{-1}, these $\chi_d(E)$ rapidly reach the asymptotic regime for $d \geqslant 1$. Thus a wide variety of physically interesting potentials, quite different as functions of r, show universal behavior of χ_d. For determining the spectra it is practically sufficient to use χ_1, χ_2, χ_3, simply associated with the total numbers of states. The above transition from $V(r)$ to χ_d may be in a sense called a 'spectral representation'.

References

[1] Bohr A and Mottelson B R 1974 *Nuclear Structure* vol 2 (New York: Benjamin) chapter 6
[2] Martin A 1986 Quarkonium *Comment. Nucl. Part. Phys.* **16** 249–67
[3] Quigg C and Rosner J L 1979 Quantum mechanics with applications to quarkonium *Phys. Rep.* **56** 167–235
[4] Grosse H and Martin A 1980 Exact results on potential models for quarkonium systems *Phys. Rep.* **60** 341–92
[5] Kotos B A and Grypeos M E 1995 Parametrization of the effective potential in sodium clusters *Atomic and Nuclear Clusters (Proc. 2nd Int. Conf. (Santorini, Greece, 28 Jun.–2 Jul. 1993))* ed G S Anagnostatos and W von Oertzen (Berlin: Springer) pp 242–5
[6] Ostrovsky V N 1997 $3n_r + l$ grouping of energy levels and clusters *Phys. Rev.* A **56** 626–31
[7] Ostrovsky V N 2001 What and how physics contributes to understanding the periodic law *Found. Chem.* **3** 145–81
[8] Block M, Drakoudis A, Leuthner H, Seibert P and Werth G 2000 Crystalline ion structures in a Paul trap *J. Phys. B: At. Mol. Opt. Phys.* **33** L375–82
[9] Franceschetti A and Zunger A 2000 Hund's rule, spin blockade, and the Aufbau principle in strongly confined semiconductor quantum dots *Europhys. Lett.* **50** 243–9
[10] Martin A 1987 Some properties of bound states in potentials *Recent Developments in Mathematical Physics (26th Int. Universitatswochen fur Kernphysik (Schladming, Austria, 17–27 Feb. 1987))* ed H Mitter and L Pittner (Berlin: Springer) pp 53–79
[11] Baumgartner B, Grosse H and Martin A 1985 Order of levels in potential models *Nucl. Phys.* B **254** 528–42
[12] Martin A 1992 Potential models: predictive rigorous results *From Superstrings to the Real Superworld: Proc. Int. School of Subnuclear Physics (30th Int. School of Subnuclear Physics 'Ettore Majorana' (Erice, Italy, 14–20 July 1992))* ed A L Zichichi (Singapore: World Scientific) pp 482–511
[13] Langer K E 1937 On the connection formulas and the solutions of the wave equation *Phys. Rev.* **51** 669–76
[14] Lobashev A A and Trunov N N 1999 *Teor. Mat. Fiz.* **120** 99
Lobashev A A and Trunov N N 1999 The reduced semiclassical description method *Theor. Math. Phys.* **120** 896–909 (Engl. transl.)
[15] Lobashev A A and Trunov N N 2000 *Teor. Mat. Fiz.* **124** 463
Lobashev A A and Trunov N N 2000 An integral semiclassical method for calculating the spectra for centrally symmetric potentials *Theor. Math. Phys.* **124** 1250–64 (Engl. transl.)
[16] Tarbeyev Yu V, Trunov N N, Lobashev A A and Kukhar V V 2002 Effective quantum number for centrally symmetric potentials *Operator Theory: Advances and Applications (Operator Methods in Ordinary and Partial Differential Equations: S Kovalevski Symp. (University of Stockholm, Jun. 2000))* ed S Albeverio, N Elander, N W Everitt and P Kurasov (Basel: Birkhäuser) pp 403–10
[17] Reed M and Simon B 1978 *Methods of Modern Mathematical Physics, Analysis of Operators* vol 4 (New York: Academic) chapter 13, section 15
[18] Eisenhart L P 1926 *Riemannian Geometry* (Princeton, NJ: Princeton University Press) section 28
[19] Berezin F A and Shubin M A 1991 *The Schrödinger Equation* (Dordrecht: Kluwer Academic) p 187
[20] Mamaeva X S and Trunov N N 2003 *Teor. Mat. Fiz.* **135** 82

Mamaeva X S and Trunov N N 2003 Wave equations in Riemannian spaces *Theor. Math. Phys.* **135** 520–30 (Engl. transl.)

[21] Gombas P 1949 *Die Statistische Theorie des Atoms und ihre Anwendungen* (Wien: Springer)

[22] Tarbeyev Yu V, Trunov N N, Lobashev A A and Kukhar V V 1997 *Zh. Eksp. Teor. Fiz.* **112** 1226
Tarbeyev Yu V, Trunov N N, Lobashev A A, and Kukhar V V 1997 Extraction of information from the periodic system of the elements as an inverse problem *J. Exp. Theor. Phys.* **85** 667–72 (Engl. transl.)

[23] Paccanoni F, Stepanov S S and Tutik R S 1993 *Level Spacings Following From the Semiclassical Representation for Regge Trajectories* (Padua: Padova University) (Preprint DFPD-93-TH-20)