

Three-dimensional confinement: WKB revisited

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An alternate formalism is developed to determine the energy eigenvalues of quantum mechanical systems, confined within a rigid impenetrable spherical box of radius r_0 , in the framework of Wentzel–Kramers–Brillouin (WKB) approximation. Instead of considering the Langer correction for the centrifugal term, the approach adopted here is that of Hainz and Grabert: the centrifugal term is expanded perturbatively (in powers of \hbar), decomposing it into 2 terms – the classical centrifugal potential and a quantum correction. Hainz and Grabert found that this method reproduced the exact energies of the hydrogen atom, to the first order in \hbar , with all higher order corrections vanishing. In the present study, this formalism is extended to the case of radial potentials under hard wall confinement, to check whether the same argument holds good for such confined systems as well. As explicit examples, 3 widely known potentials are studied, which are of considerable importance in the theoretical treatment of various atomic phenomena involving atomic transitions, namely, the 3-dimensional harmonic oscillator, the hydrogen atom and the Hulthén potential.

KEY WORDS: WKB approximation, 3-dimensional spatial confinement, radial potentials, perturbative expansion, centrifugal term, harmonic oscillator, hydrogen atom, Hulthén potential

1. Introduction

Spatial confinement of electrons in artificial nanostructures, on a scale comparable to their de Broglie wavelength, is a much talked about subject for the past decade or so [1–7]. Such *artificial atoms* as they are called because of their quantized energies, undergo radical changes in terms of both physical and chemical properties, because of their extremely small spatial dimensions, making them very useful in the study of atomic and molecular phenomena [8]. However, the problem with these so-called quantum wells, quantum wires and quantum dots is that their exact analytical treatment is not possible in most of the cases. Consequently, various approximation methods – the variational approach, the shifted $1/N$ expansion technique, the modified Airy function (MAF) method, the supersymmetric version of the same (SMAF), the Wentzel–Kramers–Brillouin (WKB) approximation, its supersymmetric version (SWKB), etc., – come into the picture [9–18]. The other option is to go for a numerical solution. Of the several approximation methods, the semiclassical WKB ap-

proximation technique is a very effective tool, yielding fairly accurate results in various quantum mechanical problems, where exact solutions are unknown or difficult to find out. This method gives a good estimate of both the energy eigenvalues as well as eigenfunctions, with the exception of the region near the classical turning points. Though this approach works well for one-dimensional problems, practical use shows that the standard leading order WKB approximation always reproduces the exact spectrum for the solvable spherically-symmetric potentials $V(r)$ if the centrifugal term

$$V_C(r) = \frac{l(l+1)\hbar^2}{2r^2}$$

is replaced by the Langer correction term [19]

$$V_L(r) = \frac{(l+1/2)^2\hbar^2}{2r^2}.$$

This modification also justifies the WKB expansion of singular potentials like that of the Coulomb potential, near the origin. However, some authors have attempted to get rid of this Langer modification (LM), based on nonlinear transformations [20] and supersymmetry [21]. Though their approach yielded results which are superior to those with LM, Coulomb-type problems did not fare well. Hainz and Grabert [22] challenged this common belief and put forward a new method to deal with centrifugal terms in the WKB approximation.

Since the semiclassical WKB approximation proceeds as a perturbation in powers of \hbar , it was argued in [22] that within this expansion, the centrifugal term can be decomposed as

$$V_C(r) = \frac{l(l+1)\hbar^2}{2mr^2} = \frac{L_0^2}{2mr^2} + \frac{\hbar L_0}{2mr^2} \quad (1)$$

with $L_0 = \hbar l$. The first term is the classical centrifugal term, while the second term is a quantum correction. Thus the quantum correction can be treated as a perturbation and expanded accordingly. Proceeding along these lines, Hainz and Grabert [22] found that the semiclassical energy eigenvalues for the hydrogen atom turned out to be exact to the first order in \hbar , with all higher order corrections vanishing. The aim of the present work is to check whether the same argument holds good for confined systems as well. The formalism of [22] is extended to the case of radial potentials confined within rigid impenetrable spheres of radius r_0 . As explicit examples, 3 widely known cases are studied, viz.,

- (i) the 3-dimensional harmonic oscillator (HO);
- (ii) the hydrogen atom;
- (iii) the Hulthén potential;

These potentials are of considerable importance in theoretical treatment of various atomic phenomena involving atomic transitions. It is observed that this formalism gives

a better estimate of the energy spectrum than the case with Langer modification, even in case of spatially confined systems.

The organisation of the paper is as follows. In section 2, the WKB formalism is extended to include quantum mechanical systems confined radially, expanding the centrifugal term perturbatively in powers of \hbar . In section 3, the approach is applied explicitly to 3 physically relevant cases, namely, the 3-dimensional harmonic oscillator, the hydrogen atom, and the Hulthén potential. Section 4 is kept for conclusions and discussions.

2. Theory

The starting point of the study is the three-dimensional Schrödinger equation for a radial potential $V(r)$

$$\frac{d^2}{dr^2}\psi(r) + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right]\psi(r) = 0, \quad (2)$$

where $l(l+1)\hbar^2$ represents the eigenvalues of the square of the angular momentum operator L^2 and m is the mass of the particle. It is worth noting here that the WKB approximation can be applied only when the de Broglie wavelength $\lambda = h/p$ ($h = 2\pi\hbar$) is changing slowly. With the help of (1) the radial Schrödinger equation (2) can be cast in the form

$$\frac{d^2}{dr^2}\psi(r) + \frac{2m}{\hbar^2}\left[E - V_{\text{eff}}(r) - \hbar\frac{L_0}{2mr^2}\right]\psi(r) = 0, \quad (3)$$

where

$$V_{\text{eff}}(r) = V(r) + \frac{L_0^2}{2mr^2}. \quad (4)$$

In order for the physical system to have a stable bound state (discrete spectrum) it must have two classical turning points r_1 and r_2 . This gives rise to 3 regions given by

- region 1: $0 < r < r_1, V_1 > E$;
- region 2: $r_1 < r < r_2, E > V_1$;
- region 3: $r > r_2, V_1 > E$,

where

$$V_1(r) = V_{\text{eff}}(r) + \hbar\frac{L_0}{2mr^2}. \quad (5)$$

If one defines $\Gamma(r)$ and $\kappa(r)$, with $(\kappa^2 = -\Gamma^2)$ by

$$\Gamma(r) = \sqrt{\frac{2m}{\hbar^2}\left\{(E - V_{\text{eff}}) - \hbar\frac{L_0}{2mr^2}\right\}}, \quad (6)$$

$$\kappa(r) = \sqrt{\frac{2m}{\hbar^2} \left\{ (V_{\text{eff}} - E) + \hbar \frac{L_0}{2mr^2} \right\}} \quad (7)$$

then (3) reduces to

$$\left\{ \frac{d^2}{dr^2} - \kappa^2(r) \right\} \psi = 0 \quad \text{in regions 1 and 3,} \quad (8)$$

$$\left\{ \frac{d^2}{dr^2} + \Gamma^2(r) \right\} \psi = 0 \quad \text{in region 2.} \quad (9)$$

Expanding in powers of \hbar , and keeping terms to the first order in \hbar , one can write $\Gamma(r)$ and $\kappa(r)$ as

$$\Gamma(r) \simeq \Gamma_0(r) - \frac{L_0}{2\hbar\Gamma_0 r^2}, \quad (10)$$

$$\kappa(r) \simeq \kappa_0(r) + \frac{L_0}{2\hbar\kappa_0 r^2}, \quad (11)$$

where

$$\Gamma_0(r) = \sqrt{\frac{2m}{\hbar^2} \{E - V_{\text{eff}}\}}, \quad (12)$$

$$\kappa_0(r) = \sqrt{\frac{2m}{\hbar^2} \{V_{\text{eff}} - E\}}, \quad (13)$$

so that

$$\frac{1}{\sqrt{\Gamma(r)}} \simeq \frac{1}{\sqrt{\Gamma_0(r)}} \left\{ 1 + \frac{L_0}{4\hbar\Gamma_0^2 r^2} \right\}, \quad (14)$$

$$\frac{1}{\sqrt{\kappa(r)}} \simeq \frac{1}{\sqrt{\kappa_0(r)}} \left\{ 1 - \frac{L_0}{4\hbar\kappa_0^2 r^2} \right\}. \quad (15)$$

The conventional WKB ansatz is assumed for the wave function:

$$\psi(r) = \exp \left[\frac{i}{\hbar} \sum (-i\hbar)^k S_k(r) \right]. \quad (16)$$

Substituting

$$y_k(r) = \frac{\partial S_k(r)}{\partial r} \quad (17)$$

and expanding them in powers of \hbar , one obtains the set of relations

$$y_0 = \pm \sqrt{2m(E - V_{\text{eff}}(r))}, \quad (18)$$

$$y_1 = -\frac{1}{2y_0} \left(y_0' + i \frac{L_0}{r^2} \right), \quad (19)$$

$$y_{2m} = -\frac{1}{2y_0} \left\{ y_m^2 + y'_{2m-1} + 2 \sum_{k=1}^{2m-2} y_{2m-k} y_k \right\}, \quad (20)$$

$$y_{2m+1} = -\frac{1}{2y_0} \left\{ y'_{2m} + 2 \sum_{k=1}^{2m-1} y_{2m+1-k} y_k \right\}. \quad (21)$$

In the above relationships, prime denotes differentiation with respect to r . Thus y_0 turns out to be the classical momentum, and

$$\begin{aligned} y_0 &= \pm i\kappa_0 \hbar && \text{in regions 1 and 3,} \\ y_0 &= \Gamma_0 \hbar && \text{in region 2.} \end{aligned}$$

So, the wave function is a linear combination of the form:

$$\psi(r) = \sum c^\pm \exp\left[\frac{i}{\hbar} \int dr y^\pm(r)\right], \quad (22)$$

where

$$y(r) = \sum (-i\hbar)^k y_k(r) \quad (23)$$

with derivatives (to the first order in \hbar)

$$\frac{d\psi}{dr} = \left(\frac{i}{\hbar} S'_0 + S'_1 \right) \psi, \quad (24)$$

$$\frac{d^2\psi}{dr^2} = \left\{ -\frac{S_0'^2}{\hbar^2} + \frac{i}{\hbar} (2S_0'S_1' + S_0'') + S_1'' \right\} \psi. \quad (25)$$

This gives the complete solution to the Schrödinger equation (to the first order in \hbar) as

$$\psi = \frac{1}{\sqrt{y_0}} \exp\left\{ \frac{i}{\hbar} \int y_0 dr - \frac{iL_0}{2} \int \frac{dr}{y_0 r^2} \right\}. \quad (26)$$

Since the radial wave function must vanish at $r = 0$, the only allowed solution in region 1 is

$$\psi_1 = \frac{A}{\sqrt{\kappa_0}} \exp\left\{ -\int_r^{r_1} \kappa_0 dr - \frac{L_0}{2\hbar} \int_r^{r_1} \frac{dr}{\kappa_0 r^2} \right\}. \quad (27)$$

Now we shall make use of the conventional connection formulae for WKB approximation at the turning point r_1 [23], namely,

$$\frac{1}{\sqrt{\kappa(r)}} \exp\left(-\int_r^{r_1} \kappa(r) dr\right) = \frac{2}{\sqrt{\Gamma(r)}} \sin\left\{ \int_{r_1}^r \Gamma(r) dr + \frac{\pi}{4} \right\}, \quad (28)$$

$$\frac{1}{\sqrt{\kappa(r)}} \exp\left(\int_r^{r_1} \kappa(r) dr\right) = \frac{1}{\sqrt{\Gamma(r)}} \cos\left\{ \int_{r_1}^r \Gamma(r) dr + \frac{\pi}{4} \right\}. \quad (29)$$

Expanding $\Gamma(r)$ and $\kappa(r)$ in terms of $\Gamma_0(r)$ and $\kappa_0(r)$, and keeping terms up to the first order in \hbar only, the connection formulae can be cast in the form:

$$\begin{aligned} & \frac{1}{\sqrt{\kappa_0(r)}} \exp\left(-\int_r^{r_1} \kappa_0(r) dr - \frac{L_0}{2\hbar} \int_r^{r_1} \frac{dr}{\kappa_0(r)r^2}\right) \\ & \simeq \frac{2}{\sqrt{\Gamma_0(r)}} \sin\left\{\int_{r_1}^r \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^r \frac{dr}{\Gamma_0(r)r^2} + \frac{\pi}{4}\right\} \end{aligned} \quad (30)$$

$$\begin{aligned} & \frac{1}{\sqrt{\kappa_0(r)}} \exp\left(\int_r^{r_1} \kappa_0(r) dr + \frac{L_0}{2\hbar} \int_r^{r_1} \frac{dr}{\kappa_0(r)r^2}\right) \\ & \simeq \frac{1}{\sqrt{\Gamma_0(r)}} \cos\left\{\int_{r_1}^r \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^r \frac{dr}{\Gamma_0(r)r^2} + \frac{\pi}{4}\right\}. \end{aligned} \quad (31)$$

The solutions to the Schrödinger equation in regions 2 and 3 are obtained by matching the WKB solutions on either side of the turning points r_1 and r_2 , with the help of the connection formulae (30) and (31). Thus the solution in region 2 comes out to be

$$\psi_2 = \frac{2A}{\sqrt{\Gamma_0(r)}} \sin\left\{\int_{r_1}^r \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^r \frac{dr}{\Gamma_0(r)r^2} + \frac{\pi}{4}\right\}. \quad (32)$$

To obtain the solution in region 3, ψ_2 is written as

$$\begin{aligned} \psi_2 &= \int_{r_1}^r \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^r \frac{dr}{\Gamma_0(r)r^2} + \frac{\pi}{4} \\ &= \int_{r_1}^{r_2} \Gamma_0(r) dr - \int_r^{r_2} \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^{r_2} \frac{dr}{\Gamma_0(r)r^2} + \frac{L_0}{2\hbar} \int_r^{r_2} \frac{dr}{\Gamma_0(r)r^2} + \frac{\pi}{4} \\ &= \left(\frac{\pi}{2} + \int_{r_1}^{r_2} \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^{r_2} \frac{dr}{\Gamma_0(r)r^2}\right) \\ &\quad - \left(\int_r^{r_2} \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_r^{r_2} \frac{dr}{\Gamma_0(r)r^2} + \frac{\pi}{4}\right) \\ &= \left(\frac{\pi}{2} + \theta\right) - B, \end{aligned} \quad (33)$$

where

$$\theta = \int_{r_1}^{r_2} \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_{r_1}^{r_2} \frac{dr}{\Gamma_0 r^2} \quad (34)$$

and

$$B = \int_r^{r_2} \Gamma_0(r) dr - \frac{L_0}{2\hbar} \int_r^{r_2} \frac{dr}{\Gamma_0 r^2} + \frac{\pi}{4}. \quad (35)$$

Substituting (33) into (32) and simplifying,

$$\psi_2 = \frac{2A}{\sqrt{\Gamma_0(r)}} (\cos \theta \cos B + \sin \theta \sin B). \quad (36)$$

Using the connection formula at the turning point r_2 , the solution in region 3 is obtained as

$$\psi_3 = \frac{2A}{\sqrt{\kappa_0(r)}} \cos \theta \exp(\sigma(r)) + \frac{A}{\sqrt{\kappa_0(r)}} \sin \theta \exp(-\sigma(r)), \quad (37)$$

where

$$\sigma(r) = \int_{r_2}^r \kappa_0(r) dr - \frac{L_0}{2\hbar} \int_{r_2}^r \frac{dr}{\kappa_0 r^2}. \quad (38)$$

Now, the WKB quantization rule is obtained by the constraint $\psi(r = r_0) = 0$, where r_0 is the radius of the confining spherical box. Two cases arise depending on the size of confinement, i.e.:

- (i) there is a single turning point within the box ($r_1 < r_0 < r_2$);
- (ii) both the turning points are within the box ($r_0 > r_2$);

thus yielding 2 different quantization rules.

Rule 1 (Extremely small confinement). The size of the box is so small that it admits only a single turning point, i.e., $r_1 < r_0 < r_2$.

This modifies the boundary condition to $\psi_2(r_0) = 0$. Hence the WKB quantization condition reads

$$\lambda_1 - \lambda_2 = \left(n + \frac{3}{4} \right), \quad n = 0, 1, 2, \dots \quad (39)$$

with

$$\lambda_1 = \int_{r_1}^{r_0} \Gamma_0(r) dr, \quad (40)$$

$$\lambda_2 = \frac{L_0}{2\hbar} \int_{r_1}^{r_0} \frac{dr}{\Gamma_0(r)r^2}. \quad (41)$$

Rule 2 (The confining box is not so small). The size of the box is such that both the classical turning points lie within it, i.e., $r_0 > r_2$.

Hence, in this case the solution of the Schrödinger equation must obey the boundary condition $\psi_3(r_0) = 0$, yielding the WKB quantization rule

$$2 \cos \theta \exp(\sigma(r_0)) + \sin \theta \exp(-\sigma(r_0)) = 0. \quad (42)$$

Quantization rules (39) and (42) enable one to determine the energy spectrum of any spatially confined, radial potential, in the framework of WKB approximation.

3. Calculations

In this section, the WKB rules so developed are used to determine the energy spectrum of 3 explicit potentials:

- (i) the 3-dimensional harmonic oscillator;
- (ii) the hydrogen atom;
- (iii) the Hulthén potential;

each confined within an impenetrable spherical box of radius r_0 . All the 3 potentials are of tremendous importance in a variety of physical problems, and have been studied widely. Units used are $\hbar = m = 1$ so that $L_0 = l$.

3.1. 3-dimensional harmonic oscillator

In this case

$$V(r) = \frac{r^2}{2}. \quad (43)$$

Hence the relationship $E - V_{\text{eff}} = 0$ gives the classical turning points at

$$r_1 = \left\{ E - \sqrt{E^2 - l^2} \right\}^{1/2}, \quad (44)$$

$$r_2 = \left\{ E + \sqrt{E^2 - l^2} \right\}^{1/2}. \quad (45)$$

Proceeding along the formalism developed above, the energy levels of the enclosed 3-dimensional harmonic oscillator are computed for various values of the confining parameter r_0 , with the help of the mathematical relationships in [24]. The results are presented in table 1, comparing the energies so obtained (with no modification of the centrifugal term) denoted by E , with those from the conventional WKB quantization rules for 3-dimensional confinement (with Langer modification), $E(\text{WKB})$ [18], the direct variational method, $E(\text{var})$ [9], and exact numerical values, $E(\text{exact})$ [9] for the enclosed 3-dimensional harmonic oscillator.

Table 1
Enclosed 3-dimensional harmonic oscillator ($n = n_r + l + 1, n_r = 0, l = 1$).

r_0	E	$E(\text{WKB})$	$E(\text{var})$	$E(\text{exact})$
1.0	10.2876	10.2643	10.3188	10.2822
1.5	4.9068	4.9084	4.9169	4.9036
2.0	3.3081 ^a	3.2490	3.2514	3.2469
2.5	2.6835	2.7079 ^a	2.6901	2.6881
3.0	2.5313	2.5310	2.5337	2.5313
4.0	2.5001	2.5001	2.5015	2.5001
5.0	2.5000	2.5000	2.5012	2.5000

^a In these cases the size of the rigid spherical box is such that the wall is close to the turning point, where the WKB approximation is not expected to give good results.

3.2. Hydrogen atom

The well-known Coulomb potential

$$V(r) = -\frac{1}{r} \quad (46)$$

is known to possess negative energies. However, spatial confinement alters this scenario. For extremely small confinement, the system is no longer bound. Conditions $E > 0$, and $E - V_{\text{eff}} = 0$ gives a single turning point at

$$r_t = \frac{\sqrt{1 + 2El^2} - 1}{2E}. \quad (47)$$

For all practical purposes, r_t is very small, and the eigenenergies of the enclosed system are obtained from the relationship (39)

$$\int_{r_t}^{r_0} \sqrt{2(E - V_{\text{eff}})} \, dr - \frac{l}{2} \int_{r_t}^{r_0} \frac{dr}{\sqrt{2(E - V_{\text{eff}})r^2}} = \left(n + \frac{3}{4}\right)\pi \quad (48)$$

with

$$V_{\text{eff}} = -\frac{1}{r} + \frac{l^2}{2r^2}. \quad (49)$$

However, for bound energies ($E < 0$), 2 cases may arise, depending on the size of the confining box: either there is only one turning point inside the box ($r_1 < r_0 < r_2$), or confining wall encloses both the turning points ($r_0 > r_2$). Let $E = -e$ and $V_{\text{eff}} = -v_{\text{eff}}$. The expression $E - V_{\text{eff}} = 0$ gives the roots at

$$r_1 = \frac{1}{2e} \left\{ 1 - \sqrt{1 - 2el^2} \right\}, \quad (50)$$

$$r_2 = \frac{1}{2e} \left\{ 1 + \sqrt{1 - 2el^2} \right\}. \quad (51)$$

The energy spectrum of the boxed-in hydrogen atom is determined with the help of the formalism developed above. The results are computed and presented in tabular form, for the 2p (table 2) and 3d (table 3) states. The energy eigenvalues calculated in this study, E , are compared with those obtained by the conventional (with LM) confined WKB approximation developed earlier $E(\text{WKB})$ [18], the direct variational method of Marin and Cruz, $E(\text{var})$ [9], Varshni's modification of Marin–Cruz approach, $E(\text{Varshni})$ [25], and the exact numerical values, $E(\text{exact})$ [25,26].

3.3. Confined Hulthén potential

Screened Coulomb potentials are of tremendous importance in atomic phenomena. The particular case studied here is the confined Hulthén potential, given by

$$V(r) = V_0 \frac{e^{-\delta r}}{1 - e^{-\delta r}}, \quad (52)$$

Table 2
Enclosed hydrogen atom – 2p-state ($n = n_r + l + 1, n_r = 0, l = 1$).

r_0	E	$E(\text{WKB})$	$E(\text{var})$	$E(\text{Varshni})$	$E(\text{exact})$
0.6	49.8448	49.3997	50.401	49.935	49.874
0.8	26.9179	26.5586	27.155	26.910	26.879
1.0	16.5063	16.2590	16.611	16.464	16.446
1.2	10.8828	10.7653	10.999	10.905	10.893
1.4	7.6209	7.4379	7.6857	7.6214	7.6138
1.6	5.5112	5.3928	5.5801	5.5347	5.5295
1.8	4.1512 ^a	4.0693	4.1675	4.1345	4.1308
2.0	3.1513	3.1010	3.1791	3.1547	3.1520
2.2	2.4469	2.4013	2.4641	2.4458	2.4438
2.4	1.9224	1.8815	1.9326	1.9187	1.9173
2.8	1.2129	1.1807	1.2157	1.2075	1.2068
3.0	0.9684	0.9420	0.9694	0.9631	0.9625
3.5	0.5466	0.5371	0.5459	0.5427	0.5424
4.0	0.2894	0.2771	0.2888	0.2872	0.2871
5.0	0.0154	0.0135	0.0155	0.0152	0.0152
7.0	-0.1687 ^a	-0.1666	-0.1748	-0.1748	-0.1749
10.0	-0.2269	-0.2256	-0.2369		-0.2377
14.0	-0.2487	-0.2484	-0.2484		-0.2491

^a See footnote to table 1.

Table 3
Enclosed hydrogen atom – 3d-state ($n = n_r + l + 1, n_r = 0, l = 2$).

r_0	E	$E(\text{WKB})$	$E(\text{var})$	$E(\text{Varshni})$	$E(\text{exact})$
1.0	29.8203	29.7306	30.234	29.979	29.935
1.5	12.5321	12.4895	12.692	12.587	12.570
2.0	6.6415	6.6064	6.7182	6.6640	6.6550
2.5	3.9882	3.9658	4.0288	3.9970	3.9920
3.0	2.5863	2.5593	2.6088	2.5887	2.5856
4.0	1.2467	1.2379	1.2532	1.2440	1.2427
5.0	0.6581	0.6489	0.6634	0.6588	0.6582
6.0	0.3617	0.3550	0.3634	0.3609	0.3607
7.0	0.1926	0.1890	0.1945	0.1933	0.1932
8.0	0.0919	0.0897	0.0928	0.0922	0.0921
10.0	-0.0140	-0.0156	-0.0141	-0.0142	-0.0142
12.0	-0.0625	-0.0626	-0.0625	-0.0625	-0.0625
14.0	-0.0862	-0.0860	-0.0862		-0.0862
16.0	-0.0939 ^a	-0.0928	-0.0982		-0.0984
20.0	-0.1079	-0.1077	-0.1076		-1.1079

^a See footnote to table 1.

where $V_0 = -Z\delta$, with Z the atomic number and δ the screening parameter. Taking $Z = 1$,

$$V_{\text{eff}}(r) = V(r) + \frac{l^2}{2r^2}. \quad (53)$$

Table 4
Confined Hulthén potential ($\delta = 0.1, n = n_r + l + 1$).

r_0	state	n_r	l	E	$E(\text{exact})$	$E(1/N)$
6	2p	0	1	-0.00782	-0.00865	-0.00294
7	2p	0	1	-0.03976	-0.04069	-0.03324
8	2p	0	1	-0.05510	-0.05783	-0.05293
9	2p	0	1	-0.06612	-0.06728	-0.06389
10	2p	0	1	-0.07196	-0.07257	-0.07008
25	2p	0	1	-0.07921	-0.07918	-0.07920
	3p	1	1	-0.01384	-0.01475	-0.01295
	3d	0	2	-0.01381	-0.01390	-0.01332
50	2p	0	1	-0.07920	-0.07918	-0.07920
	3p	1	1	-0.01598	-0.01605	-0.01578
	3d	0	2	-0.01450	-0.01448	-0.01450

Table 5
Confined Hulthén potential ($\delta = 0.2, n = n_r + l + 1$).

r_0	state	n_r	l	E	$E(\text{exact})$	$E(1/N)$
8	2p	0	1	-0.01607	-0.01731	-0.01242
9	2p	0	1	-0.02612	-0.02749	-0.02428
10	2p	0	1	-0.03389	-0.03339	-0.03118
25	2p	0	1	-0.04192	-0.04188	-0.04199
50	2p	0	1	-0.04191	-0.04189	-0.04196

Once again the energy eigenvalues are computed for different values of the confining radius r_0 and screening parameter δ , and the results presented in tabular form, in tables 4 and 5, for ease of comparison with those obtained from other approximation methods, namely, the shifted $1/N$ expansion method $E(1/N)$ [15], and exact numerical energies $E(\text{exact})$ [15].

4. Discussions and conclusions

In the present study the WKB approximation technique is used to derive an alternate formalism for quantum systems with radial potentials, confined within a rigid spherical box of radius r_0 . Instead of the conventional Langer modification, in this approach the centrifugal term is decomposed perturbatively (in powers of \hbar) into 2 terms, – the classical centrifugal potential and a quantum correction, following the analysis of Hainz and Grabert [22]. The unique advantage of this approach is that it requires no modification of the centrifugal term in the WKB expansion when applied to radial potentials. Moreover, the quantization rules follow naturally from the WKB connection formulae, and the calculations are straightforward, though somewhat lengthy.

As a testing ground, the analysis is applied explicitly to 3 widely studied confined systems, each of considerable importance in atomic phenomena, namely, the 3-dimensional harmonic oscillator, the hydrogen atom and the Hulthén potential. Each

system is confined within a rigid spherical box of radius r_0 . The spatial confinement imposes the additional boundary condition $\psi(r) = 0$ at $r = r_0$ on the radial wave function. This criterion, alongwith the WKB connection formula, gives the quantization rules for estimating the energy eigenvalues, E . For each case the results are computed and presented in tabular form, in tables 1–5, for ease of comparison with those obtained from other approximation methods, namely, the conventional WKB method for confined systems (using the Langer modification of the centrifugal term [18], variational results of Marin and Cruz [9], modified form of the same as given by Varshni [25] (in case of confined hydrogen atom), shifted $1/N$ expansion method [15] (in case of the confined Hulthén potential), and exact numerical results.

It is easy to observe from the tables 1–5, that the present formalism works quite well for all the 3 cases. The energy values are better than the conventional WKB energies (with Langer modification), as well as the shifted $1/N$ expansion results, justifying the perturbative expansion of the centrifugal term even for potentials under hard-wall confinement. In some cases these energies are even better than the variational results of Marin and Cruz [9]. This is true for most of the confining radii, except when the size of the box is close to the turning point. This is expected as the WKB approximation is not valid close to the turning points. It may be worth mentioning here that Hainz–Grabert version of the WKB method addresses primarily problems with singular potentials. Though the harmonic oscillator does not fall in this class strictly, nevertheless, the centrifugal term introduces a singularity at the origin for non-zero l . So the author found it interesting to check the behaviour of the confined harmonic oscillator under such an expansion.

Another point worth examining is the effect of the higher order terms. It was shown in [22] that in contrast to Langer modification, the higher than first order terms gave a vanishing contribution to the estimate for energy. However, this fact does not hold for confined potentials as is evident below: expanding in powers of \hbar , one obtains

$$\int_{r_1}^{r_0} \Gamma(r) dr = \int_{r_1}^{r_0} \Gamma_0(r) dr - \int_{r_1}^{r_0} \frac{L_0}{2\hbar\Gamma_0 r^2} dr - \int_{r_1}^{r_0} \frac{L_0^2}{8\hbar^2\Gamma_0^3 r^4} dr - \int_{r_1}^{r_0} \frac{L_0^3}{16\hbar^3\Gamma_0^5 r^6} dr - \dots \quad (54)$$

Proceeding along analogous lines as above it was found that the eigenvalues obtained in the lowest order became worse when higher order corrections were evaluated.

To conclude, this present analysis of perturbative decomposition of the centrifugal term into 2 parts – a classical potential and a quantum correction – plays a vital role in improving the WKB quantisation rule in the first order, thus yielding better estimates of the energy eigenvalues. Hence this formalism may be useful in determining the energy spectrum of any 3-dimensional radially-confined problem.

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