About the disposition of energy levels

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Received 1 June 2012
Published 5 November 2012
Online at stacks.iop.org/JPhysA/45/475301

Abstract
The unique properties of central potential of the form $-\beta e^{-\gamma r}$ were studied using the recently developed critical parameter technique. The particular cases of $\gamma = 0$ and $\gamma = -1$ yield, respectively, the exponential and Yukawa potentials widely used in atomic, molecular and nuclear physics. We found different behavior of the energy levels of this potential for three different ranges of the value of $\gamma$. For $\gamma \geq 0$ it was found that the energy of bound states with the same principal quantum number $N$ decreases with increasing angular momentum $\ell$. The Gaussian and Woods–Saxon potentials also show this behavior. In contrast, for $-2 < \gamma \leq -1$ increasing $\ell$ gives a higher energy, resembling the Hulthen potential. However, a potential with $-1 < \gamma < 0$ possesses mixed properties, which give rise to several interesting results. For one, the order of energy levels with different quantum numbers is not preserved when varying the parameter $\beta$. This leads to a quantum degeneracy of the states, and in fact, for a given value of $\gamma$ we can find the values $\beta_{th}$ for which two energy levels with different quantum numbers coincide. Another interesting phenomenon is the possibility, for some values of $\gamma$ in this range, for two new energy levels with different quantum numbers to appear simultaneously when $\beta$ reaches their common critical value.

PACS numbers: 03.65.Ge, 03.65.Sq, 02.30.Mv, 02.60.Lj

1. Introduction
Interest in the ordering of energy levels is as old as quantum mechanics. It can be reflected in the electron configurations of the elements in the periodic table, and in the nuclear shell model. In the 1980s there was a renewed interest in this subject following the discoveries of mesons composed of the heavier quarks $c$ and $b$. From the disposition of the energy levels of these mesons, the nature of the quark–quark (or, rather quark–antiquark) potential can be deduced, if one can relate the properties of the potential with the ordering of the energy levels pertaining to it. This development led the authors of [1] (following [2, 3]) to prove that for non-relativistic two-body systems, the order of energy levels with the same principal quantum
number $N$ is controlled by the sign of the Laplacian of the spherically symmetric potential $V(r)$,

$$\Delta V(r) = \frac{2}{r} \frac{dV}{dr} + \frac{d^2V}{dr^2}.$$  \hspace{1cm} (1)

where $N = n + \ell + 1$, $n$ is the number of nodes in the radial wavefunction and $\ell$ is the angular momentum quantum number. Specifically, they show that under the following two conditions, the ordering of energy levels with the same principal quantum number $N$ can be exactly determined\(^1\)

1. If
   $$\Delta V(r) > 0 \text{ for all } r > 0$$
   then
   $$E_{n,\ell} > E_{n-1,\ell+1}.$$  \hspace{1cm} (2)

2. If
   $$\Delta V(r) < 0 \text{ for } r < r_0, \text{ and } \frac{dV}{dr} < 0 \text{ for } r \geq r_0 > 0,$$
   then
   $$E_{n,\ell} < E_{n-1,\ell+1}.$$  \hspace{1cm} (5)

These results were also generalized for the relativistic case in [4], but in this paper we limit ourselves to the non-relativistic realm.

The question arises from these results: what can one say about the ordering of energy levels relating to potentials that do not fulfill either of conditions (2) or (4) above? In this paper we try to answer this question for the exponential-power (EP) potential, i.e. of the form

$$V_{\beta\gamma}(r) = -\beta e^{-r^\gamma} \ (\beta > 0, \gamma > -2).$$  \hspace{1cm} (6)

This is done using the critical parameter technique (CPT) recently introduced in [5], where it was also used to study the energy levels of a few short-range central potentials widely used in atomic, molecular and nuclear physics. Two of these, namely the exponential and Yukawa potentials, are special cases of $V_{\beta\gamma}$ with $\gamma$ equal to $0$ and $-1$, respectively.

The rest of this paper is organized as follows. In section 2 we give a brief summary of the CPT, and formulate a conjecture regarding the order of the energy levels, which will be addressed in the sections that follow. We also introduce a new series expansion to be used for potentials that depend on non-integer parameters. In section 3 we review the ordering of levels of the potentials studied in [5], considering the conditions given above. In section 4, we explicitly solve a counterexample that disproves the conjecture and shed light on its range of applicability. In section 5 two consequences of these results are given, and a few concluding remarks are given in section 6.

\(^1\) Note that for the second case only the weaker condition is given here, instead of the more restrictive condition, $\Delta V(r) < 0$ for all $r > 0$, which is the opposite of (2).

\(^2\)
2. Methods

In [5] the CPT was introduced as a methodology for obtaining information on the bound solutions of the non-relativistic Schrödinger equation with central potentials of the form

\[ V(r) = -V_0 f(r/r_s), \quad (V_0 > 0), \]  

where \( r_s \) is the so-called screening parameter, and \( V_0 \) represents the coupling constant. Taking into account the scaling properties, the solution of the relevant equation depends effectively on a single parameter \( \beta = \frac{2mgr_s^{2+\gamma}}{\hbar^2} \), where \( m \) is the reduced mass of the considered system. Parameter \( g \), which is proportional to \( V_0 \), will be defined in (9). The CPT consists primarily of finding at what values of \( \beta = \beta_{n,\ell} \), as it is being varied, an eigenstate of the Hamiltonian with given \{\( n, \ell \)\} becomes a transition state, i.e. will have zero energy. Further increasing \( \beta \) beyond this ‘critical’ value (CP) will make this eigenstate a bound state, causing a new bound energy level \( E_{n,\ell} \) to ‘appear’.

This technique allows one to answer such questions as: (a) how many bound states with a given \( \ell \) exist for a given potential? (b) what is the maximum \( \ell \) a bound state can have, given the potential? etc.

In [5] it is also shown that the CPT can determine the order in which the different energy levels ‘appear’, as \( \beta \) is increased. This led the authors to conjecture that this order of the energy levels is preserved when \( \beta \) is further increased beyond the values at which the levels first appeared. If this conjecture is true, then one can very easily determine the ordering of energy levels of every potential that can be solved using the CPT. For example, the authors of [5] derive the conditions (67), regarding the ordering of the energy levels of the potentials studied there, by relying only on their knowledge regarding the relations between the CPs obtained for each of these potentials. Our results suggest that the validity of the conjecture depends on the behavior of the potential near the origin, as shown in several examples below.

A few technical details are due here. All calculations were provided by the Mathematica 8 [7] codes which realized methods described in [5]. The CPs depend on the asymptotic behavior \((r \to \infty)\) of \( \chi(r) \), the solution to the corresponding Schrödinger equation

\[
\frac{d^2 \chi(r)}{dr^2} = \left[ -\beta v(r) + \frac{\ell(\ell + 1)}{r^2} - E_{n,\ell}(\beta) \right] \chi(r)
\]  

when

\[ E_{n,\ell}(\beta) \to 0. \]

However, the numerical integration of the above differential equation starts from some small value of \( r \). Therefore, the accuracy of the asymptotic behavior is defined by our possibility to calculate accurately the radial wavefunction (and its derivative) at this initial value of \( r \) which should be chosen as far as possible from the origin. Let the leading term of a series expansion for the potential under consideration have the form

\[ v(r) \simeq \frac{g}{r^{\alpha}}. \quad (g > 0, \alpha < 2). \]  

A series expansion for the reduced radial wavefunction in the case of a potential with an integer or half-integer \( \alpha \) was presented in [5]. In order to provide calculations of the CPs, e.g., for the EP potential with any real \( \gamma = -\alpha > -2 \), one needs a series expansion for the corresponding radial wavefunction. Therefore, we present such an expansion:

\[
\chi(r) = C_{\ell+1} \left( 1 + \sum_{k=1}^{\infty} \sum_{i=0}^{\infty} A_{ki}(\beta) r^{(2-\alpha) + i} \right).
\]
Here $C$ is an arbitrary constant, and the coefficients $A^{(i)}_{ki}(\beta)$ represent polynomials in $\beta$. The duplicated powers of $r$ certainly have to be dropped. Substituting equation (10) into equation (8), and then equating sequentially (starting from the lowest power) the expansion coefficients of the same powers of $r$ for the left-hand and right-hand sides, one can calculate any finite number of the coefficients $A^{(i)}_{ki}(\beta)$. This expansion can be used to solve equation (8) with or without taking the limit $E_{n,\ell} \to 0$ in order to find either the CPs or the energies $E_{n,\ell}(\beta)$, respectively.

It is interesting to note that even though the leading term of this expansion, $r^{\ell+1}$, is well known, we could not find the general form (10) in the scientific literature.

3. Cases

It is easy to check that the Hulthen and the Yukawa potentials fulfil condition (4), and therefore their energy levels should follow (5). This coincides with the results presented in [5] (see the first condition in (67) there).

In contrast, the energy levels of the exponential, the Gaussian and the Woods–Saxon potentials should satisfy inequality (3), according to the second condition of (67) in [5]. Interestingly, however, the Laplacians and the first derivatives of these potentials obey the conditions

$$\Delta V(r) \gtrless 0 \quad \text{for} \quad r \leq r_0,$$
$$dV/dr > 0 \quad \text{for all} \quad r > 0,$$

which differ slightly from (2), and in fact do not coincide with any of the conditions mentioned in [1]. Our results for these potentials satisfy inequality (3), in accord with the conjecture.

Note that the Yukawa and exponential potentials, which are the special cases with $\gamma = -1, 0$ of the EP potential (6), demonstrate opposite ordering for energy levels with equal principal quantum numbers. The Laplacian of the potential (6) has a form

$$\Delta V(r) = V(r) \left[ 1 + \frac{(\gamma + 1)(\gamma - 2r)}{r^2} \right].$$ (12)

It is easily seen that for $\gamma \leq -1$ the right-hand side of equation (12) is negative for all $r > 0$. Hence, the corresponding energy levels must satisfy inequality (5). On the other hand, it follows from the results of [5] that for $\gamma = 0$, inequality (3) holds. This is connected to the fact that the leading term in expansion of the exponential potential near the origin is proportional to zero or positive power of $r$ (such is also the case for the Gaussian and Woods–Saxon potentials, mentioned above). This behavior suggests that the potential (6) with $-1 < \gamma < 0$ may possess some mixed properties.

In order to check this we have computed the CPs for the EP potential (6) with different $\gamma$ in the range $(-1, 0)$.

2 However, most of the coefficients are monomials.  
3 Two versions of the Woods–Saxon potential with different parameters were studied in [5].  
4 It is worth noting that the potential of the form (6) was also studied by means of the so-called auxiliary field method in [6]. There, the critical parameters (or ‘critical heights’ in the language of [6]) were obtained for the exponential and the Yukawa potentials with $\ell, n \leq 3$, and within the limits of their inferior precision, coincide with the results from [5].  
5 Note that the Laplacian of the Yukawa potential ($\gamma = -1$) reduces to the Yukawa potential itself.  
6 It is easy to guess that for $\gamma > 0$, as well.
Table 1. Critical parameters $\beta_{n,\ell}$ of the EP potential (6) with $\gamma = -1/2$, $V(r) = -\beta \exp(-r)/\sqrt{r}$.

| $n$ | $\ell$ | 0   | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|-----|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1   | 1.72515| 8.77711| 20.6738| 37.4369| 59.0736| 85.5867| 116.977| 153.246| 194.393| 240.419|
| 2   | 7.95958| 19.2665| 35.3988| 56.3915| 82.2555| 112.995| 148.611| 189.105| 234.478| 284.729|
| 3   | 18.8289| 34.2285| 54.5185| 79.6946| 109.755| 144.699| 181.525| 229.232| 273.775| 327.468|
| 4   | 34.341| 53.7313| 78.1078| 107.418| 141.639| 180.761| 224.775| 273.678| 327.468| 386.142|
| 5   | 54.498| 77.8093| 106.213| 139.61| 177.956| 221.226| 269.405| 322.485| 380.46| 443.325|
| 6   | 79.3008| 106.482| 138.864| 176.307| 218.742| 266.131| 318.451| 375.687| 437.829| 504.872|
| 7   | 108.75| 139.762| 176.081| 217.532| 264.024| 315.505| 371.942| 433.313| 499.606| 570.809|
| 8   | 142.845| 177.657| 217.879| 263.306| 313.825| 369.371| 429.901| 495.388| 565.812| 641.616|
| 9   | 181.588| 220.174| 264.269| 313.642| 368.162| 427.749| 492.35| 561.931| 636.47| 715.947|
| 10  | 224.977| 267.316| 315.259| 368.553| 427.049| 490.653| 559.304| 632.961| 711.596| 795.187|
| 11  | 273.013| 319.087| 370.857| 428.048| 490.97| 558.07| 630.778| 708.493| 791.207| 878.895|
| 12  | 325.696| 375.489| 431.066| 492.134| 558.515| 630.091| 706.784| 788.538| 875.315| 967.086|
| 13  | 383.027| 436.525| 495.891| 560.814| 631.112| 706.646| 787.332| 872.432| 963.934| 1059.77|
| 14  | 445.004| 502.195| 565.336| 634.104| 708.294| 787.769| 872.432| 962.217| 1057.07| 1156.97|
| 15  | 511.629| 572.501| 639.403| 711.998| 790.068| 873.467| 962.091| 1055.87| 1154.74| 1258.67|
| 16  | 582.901| 647.445| 718.096| 794.502| 876.437| 963.745| 1056.32| 1154.07| 1256.95| 1364.91|
| 17  | 658.82| 727.027| 801.414| 881.62| 967.407| 1058.61| 1155.11| 1256.83| 1363.7| 1475.68|
| 18  | 739.386| 811.249| 899.362| 973.355| 1062.98| 1158.07| 1258.49| 1364.16| 1475.01| 1590.98|
| 19  | 824.6| 900.11| 981.94| 1069.71| 1163.16| 1262.12| 1366.45| 1476.06| 1590.87| 1710.84|
| 20  | 914.46| 993.611| 1079.15| 1170.68| 1267.95| 1370.77| 1478.99| 1592.53| 1711.3| 1835.24|

4. A counterexample

The CPs for the EP potential with $\gamma = -1/2$ are presented in table 1. One can observe that the critical parameters $\beta_{n,\ell}$ and $\beta_{n-1,\ell+1}$ (that relate to the same principal quantum number $N$) are on the diagonals connecting the $\{n, \ell\}$-positions assigned as $\{n, 0\}$ on the lower left and $\{1, n-1\}$ on the upper right. The smallest parameter $\beta_{\text{min}}$ of each diagonal was framed\(^7\).

\(^7\) It is seen that the smallest parameters occupy the positions $\{n, l\}$ with $n = 2l + p$, where $p = 1, 2, 3$. 

5
The critical parameters determine the order in which the energy levels appear. According to the conjecture formulated in section 2, it is 'naturally' assumed that this order is preserved when the parameter $\beta$ of the EP potential (6) is increased.

If this assumption is true, the energy levels $E_{n,\ell}(\beta)$ corresponding to $\beta > \beta_{n,\ell}$ must satisfy inequality (5) for $[n, \ell]$ belonging to CPs which are framed or are above the framed ones. In contrast, the energy levels for the CPs which are below the framed ones must obey inequality (3).

The computational results presented in table 2 show that this assumption does not hold here. It follows from table 1 that for the EP potential (6) with parameters $\gamma = -1/2$ and $\beta > 194.393$, the Schrödinger equation (8) has bound state solutions only for $\ell \leq 8$ and $n \leq (9 - \ell)$. The corresponding binding energies $E_{n,\ell}$ presented in table 2 were computed by two methods for fidelity. First, the results were obtained by solving equation (8) directly. Then, an application of the technique presented in [8] enabled us to verify the accuracy of these results. Table 2 demonstrates that only the four energy levels $E_{n,\ell}(200)$ with $n + \ell = 9$ and $5 \leq \ell \leq 8$ satisfy inequality (5), whereas levels with $0 \leq l \leq 5$ (and the same $N = 10$) fulfil the opposite condition (3). This contradicts the assumption, and disproves the conjecture.

Where does it fail? For the conjecture to hold, the energy levels must retain the order in which they appear, as the universal parameter $\beta$ is increased. Obviously, all existing energy levels are lowered when $\beta$ increases, until a new level appears. However, for the EP potential (6) with $-1 < \gamma < 0$ the 'speed of lowering' the energy levels $E_{n,\ell}$ and $E_{n',\ell'}$ with $\delta = n - n' = \ell' - \ell = \pm 1$ (and the same $N$) is opposite to the order of their appearance in this process. That is, a level $E_{n,\ell}$ that has just appeared will be going down in energy 'faster' than the originally lower level (with the same $N$ and $\delta = \pm 1$) that had appeared before it. Therefore, at some value of $\beta = \beta_{thr}^{(n,\ell)}$ these levels will reverse their order.

### 5. Degeneracy and simultaneous appearance

The fact that the 'speed of lowering energy' of the levels that had just appeared is higher than that of levels with the same $N$ and $\delta = \pm 1$ but that had appeared beforehand has several interesting consequences.

First of all, as suggested above, this behavior will cause a degeneracy of two energy levels $E_{n,\ell} = E_{n-1,\ell+1}$, when $\beta$ reaches the value for which these two levels reverse their order. Indeed, for the example above (with $\gamma = -1/2$ and $\beta > 194.393$), at some threshold $\beta = \beta_{thr}^{(3,6)}$ the energy $E_{4,5}(\beta_{thr}^{(3,6)})$ becomes equal to $E_{3,6}(\beta_{thr}^{(3,6)})$. The further increase of $\beta$ to $\beta_{thr}^{(2,7)} > \beta_{thr}^{(3,6)}$ leads to $E_{2,7}(\beta_{thr}^{(2,7)}) = E_{3,6}(\beta_{thr}^{(2,7)}) < E_{4,5}(\beta_{thr}^{(2,7)})$. At last, for some

### Table 2. Binding energies $-E_{n,\ell}$ for the EP potential $V(r) = -200 \exp(-r)/\sqrt{r}$. 

| $n$ | $\ell$ |
|-----|-------|
| 0   | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     |
| 1   | 453.076 | 253.517 | 161.668 | 106.560 | 69.5605 | 43.3235 | 24.2864 | 10.5122 | 0.943 082 |
| 2   | 217.692 | 142.656 | 95.1156 | 62.4832 | 39.1216 | 22.1330 | 9.896 29 | 1.526 00 |
| 3   | 123.435 | 83.5646 | 55.2885 | 34.7710 | 19.7922 | 9.041 98 | 1.790 35 |
| 4   | 71.9016 | 48.0047 | 30.3073 | 17.3037 | 7.998 82 | 1.810 80 |
| 5   | 40.6508 | 25.7661 | 14.7085 | 6.812 96 | 1.647 54 |
| 6   | 21.1813 | 12.0487 | 5.531 20 | 1.354 10 |
| 7   | 9.369 62 | 4.202 50 | 0.982 547 |
| 8   | 2.882 04 | 0.587 78 |
| 9   | 0.234 38 |
\( \beta = \beta_{\text{thr}}^{(1,8)} \) for which two new levels \( \beta_{\text{thr}}^{(1,8)} < \beta < \beta_{1,9} \) all possible energy levels with \( N = 10 \) satisfy condition (3). The situation is of course similar for smaller \( \beta \). The corresponding \( \beta_{\text{thr}} \) are presented in table 3, where \( \ell_{\text{max}} \) is the largest orbital number which admits a bound state for the given parameter \( \beta = \beta_{\text{thr}} \). It is seen that for \( \tilde{N} = \ell_{\text{max}} + n = 8, 9 \) there are three threshold potentials \( (n = 1, 2, 3) \) for each \( \tilde{N} \). For \( \tilde{N} = 5, 6, 7 \) there are only two threshold potentials \( (n = 1, 2) \) for each \( \tilde{N} \). At last, for \( \tilde{N} = 2, 3, 4 \) one obtains the threshold potentials producing the pairs of states with \( E_{3d}(\beta_{\text{thr}}^{(1,1)}) = E_{3d}(\beta_{\text{thr}}^{(1,8)}), E_{4d}(\beta_{\text{thr}}^{(1,2)}) = E_{4d}(\beta_{\text{thr}}^{(1,3)}) \) and \( E_{5f}(\beta_{\text{thr}}^{(1,3)}), E_{5f}(\beta_{\text{thr}}^{(1,8)}) \) with the same principal quantum numbers. Here we used the widespread notation for \( E_{N,\ell} \equiv E_{n, l} \).

The second consequence of this behavior is the possibility for simultaneous appearance of two levels, i.e. there are certain values of \( -1 < \gamma < 0 \) for which two new levels \( E_{n, \ell} = E_{n-1, \ell+1}(\approx -0) \) ‘appear’ simultaneously at the same value \( \beta_{n, \ell} = \beta_{n-1, \ell+1} \). Our computations show that, e.g.,

\[
\beta_{2, 0} = \beta_{1, 1} \approx 7.9797 \quad \text{for} \quad \gamma = -0.238825, \tag{13}
\]

\[
\beta_{3, 0} = \beta_{2, 1} \approx 19.1036 \quad \text{for} \quad \gamma = -0.42046, \tag{14}
\]

and so on.

How does this behavior depend on the parameters of the potential (6)? Recall that the framed values in table 1 represent the smallest \( \beta \) for all levels with the same \( N \) and \( \delta = \pm 1 \). For \( \gamma = -1/2 \) they are situated along the ‘diagonal’ curve of the table. As \( \gamma \) approaches 0, the curve of framed (smallest) \( \beta \) approaches the lower left corner. At the limit \( \gamma = 0 \) all the potentials will satisfy (3), regardless of \( \beta \). In contrast, as \( \gamma \) approaches \(-1\), the curve of smallest \( \beta \) approaches the upper right corner, and at the limit \( \gamma = -1 \) all the potentials will satisfy (5).

Also note that beyond these limits \( (\gamma \leq -1, \text{ or } \gamma \geq 0) \) the ‘speed of lowering energy’ of the levels with the same \( N \) and different \( \ell \) now matches the order of their appearance. This is related to the behavior of the potential near the origin. As was mentioned above, this is the reason why the exponential, Gaussian and Woods–Saxon potentials satisfy (3), even though they only fulfil conditions (11) rather than (2).

6. Conclusions

We have used the CPT developed in [5], together with a new series expansion for the radial wavefunction (10), to study the ordering of energy levels with the same principal quantum number \( N \) for a central potential of the form (6), as well as for several other short-range central potentials widely used in different fields of physics. We found that our results are not only consistent with the conditions formulated in [1], but they even suggest a possible generalization of condition (2) to (11). We found that the ordering of levels of the potential (6) can be characterized according to three ranges of the values of the parameter \( \gamma \)
Although it was not shown explicitly, these different properties are related to the behavior of the potential near the origin, and perhaps this rule can also be generalized to other potentials.

In the range $-1 < \gamma < 0$ the above properties give rise to several interesting consequences for the EP potential (6), such as the degeneracy of two (or more) energy levels $E_{n,\ell}(\beta) = E_{n-1,\ell+1}(\beta)$ at some calculable values of $\beta = \beta_{\text{thr}}$, or the simultaneous appearance of two new energy levels (as transition states, cf [5]) at the same value of the critical parameter $\beta = \beta_{n,\ell} = \beta_{n-1,\ell+1}$.

Acknowledgment

This work was supported by the Israel Science Foundation grant 954/09.

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