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The energy levels of the sextic double-well potential

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Abstract. An infinite set of exact solutions of the sextic double-well potential is derived. These solutions that are obtained for special configurations of the well are shown to provide an excellent description of the entire negative energy spectrum for arbitrary geometry of the well. A universal feature of this class of deep double-well potentials is deduced.

1. Introduction

Double-well potentials are of interest in many branches of physics. Unfortunately, only a few selected problems of this class are exactly solvable. A well known solvable case due to Merzbacher (1970) is that of two parabolic wells. Others include the case of a rectangular double well and a combination of two δ -function wells. Thus, the energy spectrum has to usually be found using numerical techniques or by approximation methods. A number of very ingenious approximation techniques now exist, such as the two-step procedure of Chen and Cheng (1984) and the rational function approach of Fernandez *et al* (1989). The quantity of great interest is the splitting between the two lowest-lying levels which controls the tunnelling rate from one well to the other. This splitting is known to be a very sensitive function of the parameters of the well. The wkb based calculation of Landau and Lifshitz (1977) suggests that it has an exponential character. The solvable cases confirm this and so do the variational calculations in specific instances. However, supersymmetry based calculations of Cooper *et al* (1987) indicate that this may not always be the case.

In this work we examine the one-dimensional double-well potential $V = -ax^2 + bx^6$ ($a, b > 0$ and for convenience we set $a = \frac{1}{2}m\omega^2$). We shall show that this problem has an infinite set of exactly derivable solutions that are obtained for a specific set of values of a suitable coupling constant ratio (denoted by β in the sequel) but which are such as to determine the entire negative energy spectrum (whenever it exists) very accurately. A partial but exact set of positive energy solutions also materialise. A remarkable feature of these solutions is that they either have energy $E = 0$ or appear in pairs $\pm E$. A general feature of all double-well potentials of the type $V = -ax^2 + bx^{2s}$, $s = 2, 3, 4 \dots$, will also be deduced.

The paper is divided into three main sections. In section 2 we present the exact set of solutions for specific sextic double-well geometries, i.e., for a tuned set of β values and assemble their main consequences. Section 3 extends the results to a well of

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arbitrary geometry through a suitable interpolation scheme. Section 4 is reserved for concluding remarks and general observations.

2. The exact solutions

Using dimensionless variables the Schrödinger equation reads

$$\psi'' + (\varepsilon + y^2 - \beta^2 y^6)\psi = 0. \quad (1)$$

Here, $y = \alpha x$, $\alpha^2 = \hbar / m\omega$, $\varepsilon = 2E / \hbar\omega$, $\beta^2 = 2b\hbar^2 / m^3\omega^4$ and primes denote derivatives with respect to y . Setting $\psi = e^{-\beta y^4/4} v(y)$ we have the equation

$$v'' - 2\beta y^3 v' + [\varepsilon + (1 - 3\beta)y^2]v = 0. \quad (2)$$

One notices that under the transformations $y \rightarrow iy$ and $\varepsilon \rightarrow -\varepsilon$, (2) remains invariant and the exponential factor $e^{-\beta y^4/4}$ is unaffected. Thus, if $\psi(y)$ is a solution of (1) with energy ε then $\psi(iy)$ is also a solution with energy $-\varepsilon$. The formal solutions of (1) thus appear in pairs $\pm\varepsilon$ unless $\varepsilon = 0$ in which case $\psi(y)$ and $\psi(iy)$ cannot be distinct since the problem is one dimensional. Hence, for $\varepsilon = 0$, the power series for $v(y)$ must be a series in powers of y^4 . Incidentally, this feature of pairing is not unique to this particular potential. Any combination of power-law potentials of the type x^{4s+2} , $s = 0, 1, 2, \dots$ has this property. But the two members of the pair need not always belong to the physical Hilbert space. Consider the simplest example where the solutions formally appear in pairs, namely the oscillator potential. Here, the transformations $y \rightarrow iy$ and $\varepsilon \rightarrow -\varepsilon$ lead the wavefunction out of the physical Hilbert space due to the behaviour of the associated exponential factor. The minimum requirement for both members of a pair to be simultaneously physical is that the most dominant term in the potential should correspond to s odd. Even if s is odd all pairs cannot be physical. This follows due to the fact that the double-well energy spectrum is bounded from below but not from above. In the case in hand we shall find that whenever v is a polynomial the expected pairs do indeed appear and so do the zero energy solutions. Returning to (2) and introducing a second-scale transformation $y \rightarrow y(1/2\beta)^{1/4}$ we now have the equation

$$v'' - y^3 v' + (\lambda + ky^2)v = 0 \quad (3)$$

where $\lambda = \varepsilon/\sqrt{2\beta}$ and $\beta \equiv 1/(2k+3)$. This equation admits polynomial solutions for $k = 0, 1, 2, \dots$. To see this, set

$$v = \sum a_n y^n \quad (4)$$

with either $a_0 \neq 0, a_1 = 0$, or $a_0 = 0, a_1 \neq 0$. Thus, n is either even or odd. We find the three-term recursion relation

$$(n+3)(n+4)a_{n+4} + \lambda a_{n+2} + (k-n)a_n = 0. \quad (5)$$

The coefficients being successive, polynomial solutions of degree l are obtained if

$$a_l \neq 0 \quad \text{but} \quad a_{l+2} = a_{l+4} = 0. \quad (6)$$

Together, these conditions imply $k = l$. This is a necessary condition for v to be a polynomial. Hence, polynomial solutions require

$$k = 0, 1, 2, \dots \quad (7)$$

i.e.,

$$\beta = \frac{1}{3}, \frac{1}{5}, \frac{1}{7}, \dots \tag{8}$$

The condition $a_{i+2} = a_{k+2} = 0$ is equivalent to the vanishing of a $(m+1) \times (m+1)$ tridiagonal determinant whose diagonal elements are λ and whose other non-zero elements are given by

$$a_{i+i} = 2(m-i-1) \quad a_{ii+1} = 2i(2i-1) \quad \text{for } k = 2m, m = 0, 1, 2, \dots \tag{9a}$$

and by

$$a_{i+i} = 2(m-i-1) \quad a_{ii+1} = 2i(2i+1) \quad \text{for } k = 2m+1. \tag{9b}$$

Equation (9a) applies for k even and (9b) for k odd. To get some feeling for the results it is best to consider some explicit examples.

(i) $k = 0, \beta = \frac{1}{3}$. We have $\lambda = 0, v \sim y$. Hence, the ground state is at $\epsilon = 0$. For $\beta \geq \frac{1}{3}$ there are no negative levels.

(ii) $k = 1, \beta = \frac{1}{5}$. Again $\lambda = 0, v \sim y$. The one node solution has $\epsilon = 0$. Thus, for $\frac{1}{3} > \beta \geq \frac{1}{5}$ there is one and only one negative energy level with even parity.

(iii) $k = 2, \beta = \frac{1}{7}$. We have $\lambda^2 = 2 \Rightarrow \epsilon_{\pm} = \pm\sqrt{\frac{2}{7}}$ with $v_{\pm} \sim (1 \mp y^2)$. ϵ_{-} is the ground state energy and ϵ_{+} that of the two-node level. There is clearly a second negative-energy level with one node since the one-node level which was at $\epsilon = 0$ for $\beta = \frac{1}{3}$ must move downwards. Hence, for $\frac{1}{5} \leq \beta < \frac{1}{7}$ the well develops one pair of negative energy levels.

(iv) $k = 3, \beta = \frac{1}{9}$. We have $\lambda^2 = 12 \Rightarrow \epsilon_{\pm} = \pm\sqrt{\frac{12}{9}}$ with $v_{\pm} \sim (y \mp \frac{1}{3}y^3)$. The function v has one node while v_{+} has three nodes. The only odd parity level of negative energy corresponds to a polynomial solution. Shortly, we shall see that there still is only one pair of negative levels.

(v) $k = 4, \beta = \frac{1}{11}$. $\lambda = 0$ or $\lambda^2 = 32$. For $\epsilon = 0, v \sim (1 - \frac{1}{3}y^4)$. This solution has two nodes. Hence, the two-node solution at $\beta = \frac{1}{9}$ has positive energy. We still have just one pair of negative levels. The other two levels with $\lambda^2 = 32$ have $\epsilon_{\pm} = \pm\sqrt{\frac{64}{11}}$ and $v_{\pm} \sim (1 \mp 2\sqrt{2}y^2 + y^4)$. v_{-} is the nodeless solution and v_{+} has four nodes. Again no negative energy level of even parity is a non-polynomial.

(vi) $k = 5, \beta = \frac{1}{13}$. $\lambda = 0$ or $\lambda^2 = 64$. The solution for $\epsilon = 0$ is $v \sim y(1 - \frac{1}{3}y^4)$. It has three nodes. Thus, for $\frac{1}{11} \leq \beta < \frac{1}{13}$, there are three negative levels. $\lambda^2 = 64 \Rightarrow \epsilon_{\pm} = \pm\sqrt{\frac{128}{13}}$ with $v_{\pm} \sim (y \mp \frac{4}{3}y^3 + (\frac{1}{3}y^5))$. v_{+} has five nodes and v_{-} has one. No negative level of odd parity is a non-polynomial.

This process can be continued indefinitely. However, the task becomes increasingly tedious. Fortunately, the structure of (9a) and (9b) offers a simple alternative. The desired values of λ are just the eigenvalues of the corresponding matrices with diagonal elements zero. In this way we have worked out the solutions for up to $k = 100$. Going beyond this leads to no additional valuable information and consumes too much computer time. These results confirm the trends that have already been noticed and allow one to draw several general conclusions. Most importantly they lead to a very simple procedure for determining the energy spectrum for arbitrary β very accurately. Observe that the totality of the $\epsilon = 0$ solutions follow immediately by noting that the recursion relation (5) reduces to a two-step relation in this case so that one has simply the relation

$$(n+3)(n+4)a_{n+4} + (k-n)a_n = 0. \tag{10}$$

Hence, normalisable solutions for $\epsilon = 0$ are obtained for only $k = 4m$ or $k = 4m+1, m = 0, 1, 2, \dots$. The two sets of solutions have even and odd parity respectively.

The set of exact results can be summarised as follows.

(a) The number of negative levels is controlled entirely by the dimensionless coupling constant ratio β .

(b) There are no negative levels for $\beta > \frac{1}{3}$.

(c) There are no polynomial solutions for $k < 0$, i.e. $\beta > \frac{1}{3}$.

(d) For $k = 2m, m = 0, 1, 2, \dots$ there are $(m+1)$ polynomial solutions of even parity. These are the set of lowest energy even parity solutions. They are a set of orthogonal functions with a weight factor of $e^{-\beta x^4/4}$.

(e) Similarly for $k = 2m+1$, there are $(m+1)$ odd parity polynomial solutions which exhaust the lowest energy odd parity solutions.

(f) New negative levels of even parity appear whenever k increases through $4m$. Similarly, new negative levels of odd parity appear whenever k exceeds $4m+1$. No additional negative levels are obtained for any other value of k .

(g) A level of even parity appears at $\varepsilon = 0$ whenever $k = 4m$. It has $2m$ nodes. A level of odd parity appears at $\varepsilon = 0$ for $k = 4m+1$. It has $2m+1$ nodes. The appearance of a set of orthogonal polynomials for integral k has its origin in an underlying symmetry. For arbitrary β the Hamiltonian has no special symmetry but for $\beta = 1/(2k+3)$, $k = 0, 1, 2, \dots$ it develops a close connection with an underlying $SL(2, R)$ symmetry and the set of orthogonal polynomials correspond to various finite-dimensional representations of the $SL(2, R)$ group. This has been noted by Morozov *et al* (1989) for the even parity solutions.

(h) For any given integral value of k , the level separation between the levels of one parity decreases as we move up the spectrum to $\varepsilon = 0$. Beyond $\varepsilon > 0$ this trend is exactly reversed. However, up to the energies for which polynomial solutions are available the expected $n^{3/2}$ (n = single quantum number available for this problem), scaling is certainly not in evidence. For example, for $k = 100$, one finds that the lowest 25 levels of positive energy do not reflect a wkb type scaling.

(i) The behaviour of any negative level with decreasing β , i.e. increasing k , has a universal character independent of its nodal classification. Designating a level of fixed number of nodes as ε_k one finds that ε_k varies practically linearly as k for large enough k . The larger the number of nodes the larger is the value of k for which linearity sets in. In the linear regime each straight line has the same slope that very nearly equals the change in well depth per k . We shall see in the next section that this is a very valuable piece of information. First, let us explain its origin by examining the various energy scales that can contribute to the energies. The problem has two basic energy scales $\hbar\omega$ and $(b\hbar^6/m^3)^{1/4}$. Combining these two scales, a variety of other scales can be constructed, some singular and some non-singular. These scales can contribute to the energy, in principle. We can also construct an energy scale $(a^3/b)^{1/2}$ which is both classical and singular. It is readily seen that this scale alone determines the depth of the well. Naturally, therefore, such a scale can contribute directly to the energies, in spite of being singular. As $\beta \rightarrow 0$ or $k \rightarrow \infty$, it can be verified that this energy scale dominates over any other constructible scale. Thus, the depth of the well and the most dominant contribution to energy are proportional to the same scale. This culminates into the linear behaviour of ε_k in k as $k \rightarrow \infty$. Now it will be easily recognised that this feature is in fact true of all double-well potentials of the type $v = -ax^2 + bx^{2S}$. For $b \rightarrow 0$, the classical scale dictates energy as well as the depth of the well. Thus, linearity is a feature common to all such deep double-wells. Indeed, we have checked this to be true of the double-well potential $v = -ax^2 + bx^4$ by using a fifth-order Runge-Kutta method. Such a feature is fully substantiated by variational calculations.

3. Negative energy spectrum for arbitrary β

We now address ourselves to the vital question, namely, how can one exploit the set of exact results for the specific or tuned values of β to determine the energy function for arbitrary β (at least for any $\beta < \frac{1}{3}$ so that negative levels exist). First, we make two general observations.

(1) We know $\varepsilon(\beta)$ for a set of β values. This sequence of β values has a limit point. There is no reason to expect $\varepsilon(\beta)$ to become discontinuous for any $\beta \neq 0$. Hence, in principle there should be no difficulty in extending $\varepsilon(\beta)$ away from the tuned set of β values.

(2) The wavefunctions are known at the tuned set of β values. Hence, suitable variational trial functions near each such β values can be readily written down and a one- or two-parameter variational calculation should provide an excellent account of energy in the neighbourhood of the tuned set of β values. For small β one thus has a very useful approach in hand.

However, in view of the discussion presented towards the end of section 2, a very simple interpolation scheme is already available. We have noted that for small β , $\varepsilon(\beta)$ varies as $1/\beta$, i.e. ε_k varies as k . In table 1 we present a selection of results for the ground and first-excited states for the range $k = 0$ to $k = 50$. Using this we can immediately convince ourselves of the accuracy of the linear approximation. Consider, for example, the ground state and take a very extreme example. We find that $(\varepsilon_{10} + \varepsilon_{50})/2 \approx -22.294$ while from the same table $\varepsilon_{30} \approx -22.275$. It is correct to about one part in one thousand. However, in practice, we need to invoke linearity only over the range $\Delta k = 2$ and not over $\Delta k = 40$ as in the example above. This increases the accuracy substantially. For example, one finds $(\varepsilon_{28} + \varepsilon_{32})/2 \approx -22.274$ which is in excellent accord with ε_{30} . For larger values of k the accuracy of the linear approximation improves rapidly. The same is true for the one node level as well as the others. It is remarkable that even for low values of k the predictions of the linear approximation are substantially correct. In the worst case it predicts the ground state for $k = 1$ at $(\varepsilon_0 + \varepsilon_2)/2 \approx -0.535$ whereas numerically ε_1 is at about -0.515 . We thus find that the set of exact levels for tuned β does indeed determine the entire negative spectrum to an excellent approximation. To be precise, all levels lying below a small strip of width $\sim \hbar\omega$ below $\varepsilon = 0$ are predicted to an excellent approximation by the linear interpolation scheme.

Although the linear approximation over ranges of $\Delta k = 2$ fixes the absolute values of energy very satisfactorily and its accuracy increases rapidly as $\beta \rightarrow 0$, it is not very effective in estimating the splittings between the ground and first excited states. The splitting decreases far too rapidly with increasing k for the linear approximation to keep pace with it. The lack of continuity of the derivative $\partial\varepsilon_k/\partial k$ admitted by the linear approximation seems to be the source of the trouble.

The most logical, but at the same time perhaps too ambitious, way out of this difficulty is the following. Consider a large value of k , say $k = 100$. We know the lowest fifty levels of even parity exactly. Try to guess the function $\varepsilon(n)$ of the single quantum number n present in this problem that can reproduce these exact results. In addition we also know that for $n \rightarrow \infty$, the energy should scale as $n^{3/2}$. However, we have not succeeded in this venture; $\varepsilon(n)$ is certainly not an easily tractable function of n .

The next option is to plot ε_k for a fixed number of nodes as a function of k and try to guess the functional form of the curve that rapidly approaches a straight line for large k . One way is to use suitable Padé approximants. We have analysed the ground state case in detail and in fact by trial and error we have been able to find a

Table 1. Exact results for the ground state energy (ϵ_0) and the first excited state energy (ϵ_1)

k	$-\epsilon_0$	k	$-\epsilon_1$
0	0	1	0
2	1.069 044 967 649 698	3	1.632 993 161 855 452
4	2.412 090 756 622 109	5	3.137 858 162 210 945
6	3.892 995 957 870 921	7	4.646 598 402 516 486
8	5.405 411 593 010 458	9	6.165 943 251 805 180
10	6.928 294 595 884 278	11	7.691 841 292 527 599
12	8.456 356 653 030 063	13	9.221 619 414 070 378
14	9.987 484 563 854 046	15	10.753 838 413 075 24
16	11.520 595 384 884 44	17	12.287 688 485 080 67
18	13.055 064 898 734 39	19	13.822 682 311 924 02
20	14.590 506 453 699 66	21	15.358 509 260 896 84
22	16.126 667 534 625 35	23	16.894 961 928 541 28
24	17.663 376 180 603 11	25	18.431 896 521 516 42
26	19.200 511 214 456 22	27	19.969 210 193 187 68
28	20.737 984 774 895 38	29	21.506 827 430 309 34
30	22.275 731 598 214 58	31	23.044 691 534 653 30
32	23.813 702 189 474 92	33	24.582 759 104 615 42
34	25.351 858 329 769 25	35	26.120 996 352 079 19
36	26.890 170 037 197 89	37	27.659 376 579 631 43
38	28.428 613 460 702 17	39	29.197 878 412 800 68
40	29.967 169 388 855 72	41	30.736 484 536 154 19
42	31.505 822 173 805 08	43	32.275 180 773 268 23
44	33.044 558 941 473 11	45	33.813 955 406 133 73
46	34.583 369 002 933 67	47	35.352 798 664 309 14
48	36.122 243 409 601 88	49	36.891 702 336 391 36
50	37.661 174 612 843 67	51	38.430 659 470 941 76

very effective description of this curve. We use a three-parameter fit that estimates the energy to an accuracy sufficient for obtaining the splittings accurately. We employ the method of splines and parameterise the ground state as

$$\epsilon_k = \alpha k \left[1 - \frac{A_k}{B_k + k^{\gamma_k}} \right]$$

where $\alpha = 4/3\sqrt{3}$ is the slope of the straight line representing the well depth as a function of k . The parameters A_k , B_k and γ_k are determined as follows. Select an initial interval say, for example, from $k = 20$ to $k = 24$. Using the exactly known values ϵ_{20} , ϵ_{22} and ϵ_{24} determine A_k , B_k and γ_k (assumed fixed over this interval). Determine $\partial\epsilon_k/\partial k$ at $k = 20$ and $k = 24$. Next, consider the interval $k = 20$ to $k = 18$. Using $\partial\epsilon_k/\partial k|_{k=20}$, ϵ_{20} and ϵ_{18} , determine A , B , γ for this interval and so on. Similarly, we can move upwards from $k = 24$. Let us now list some illustrative examples of this fit. For $k = 7$, we now predict the ground state to be at $\epsilon \approx -4.64730$. Numerically (fifth-order Runge-Kutta) $\epsilon_N \approx -4.64727$. The linear approximation gives $\epsilon_L \approx -4.6492$. For $k = 9$ we now predict $\epsilon \approx -6.16601$ while $\epsilon_N \approx -6.16599$ and $\epsilon_L \approx -6.16685$. The improvement is significant enough to provide a good estimate of splitting recalling that the one-node levels for $k = 7$ and $k = 9$ are at $\epsilon \approx -4.646598$ and $\epsilon \approx -6.165943$ respectively. A similar fit applies to the one-node level.

On the basis of our results we can confidently state that the splitting is a very sharply decreasing function of k . For a deep well it could quite possibly be an

exponentially decreasing function of k . An exponential dependence is indeed very strongly suggested by a two-parameter variational calculation based on the trial functions

$$\Psi_{0,1} \sim e^{-\alpha(x-\gamma)^2} \pm e^{-\alpha(x+\gamma)^2}$$

for the ground and first-excited states done on the assumption that the well is very deep, that is γ is large. Incidentally, such a calculation also confirms that as $\beta \rightarrow 0$ the most dominant contribution to energy is controlled by the classical scale $(a^3/b)^{1/2}$ as remarked on in section 2. An additional qualitative reason can be cited to motivate the exponential character of splitting for $\beta \rightarrow 0$. As noted above, for $\beta \rightarrow 0$, the deep levels maintain an almost fixed distance from the bottom of the well. Effectively, such levels can be described by considering a Merzbacher-type double well with the separation between its minima equalling $(16/3\beta^2)^{1/4}$ and the effective ω computed from the known energy gap between the ground state and the bottom of the well. But the splitting between the lowest levels of such a deep parabolic double well is well known to have an exponential character. Further more, the two arguments given above are clearly valid for all double wells of the type $V = -ax^2 + bx^{2.5}$.

4. Concluding remarks

The principal feature of this work is the following. For integral k , one easily derives a partial set of manifestly normalisable solutions. The rest of the solutions for all k are, formally, power-series solutions that do not permit an easy implementation of the quantisation condition (the square integrability criterion) within our framework. However, the point is that the results for integral k that are in hand, already suffice to determine the negative energy spectrum and hence the splittings quite accurately, irrespective of the value taken by k . Besides the numerical illustrations quoted in section 3 we have also verified our energy predictions for a sample of non-integral k values to be in excellent accord with Runge-Kutta results.

Our procedure provides a straightforward guide to suitable variational functions that can also be used to estimate energies. It is worth pointing out that an accurate knowledge of energy levels does not permit us to deduce the wavefunctions via the recursion relation. This is so because the Schrödinger equation admits normalisable solutions for exact energy eigenvalues only. These we do not possess in general. Hence, a very challenging independent study that would first ascertain energy as a function of k , presumably by exploiting the information available for integrally spaced k values, deserves attention.

It is of some interest to note that the vibrational energy levels of the N atom in the ammonia molecule are well described by assuming a double-well potential of depth 0.254 eV and the separation of minima of about 0.75 Å. This well supports the three pairs of negative levels. The top-most of these levels lies very nearly at $\epsilon = 0$. For the sextic double well we find that such a configuration corresponds to $k \geq 9$ or $\beta \geq \frac{1}{21}$. The correct well depth requires the choice $\hbar\omega \approx 0.635$ eV.

Next, we note that polynomial solutions arising out of a three-step relation have been noted in many contexts. A class of such problems for example, has been listed by Calogero (1979). Such solutions are obtained for some specific values of a suitable coupling constant ratio. That they are normalisable may not necessarily suffice in every such case to guarantee that they are physical. It is easy to construct divergent solutions

for combinations of potentials which for some specific choices of suitable coupling constant ratio can become polynomials and hence normalisable. Upon lifting the tuning condition such solutions continue along a divergent path in parameter space. Such a spurious set of solutions can in fact be constructed even in the present case. Thus, as a general rule, whenever polynomial solutions result due to the tuning of a parameter, one must ensure that they are physical. In the present example this is certainly true. The origin of these solutions as noted already lies in the sudden emergence of $SL(2, R)$ symmetry of the associated Hamiltonian. Secondly, a numerical study based on a fifth-order Runge-Kutta method confirms these solutions and their smooth continuation away from the tuned values. Lastly, the energies predicted for arbitrary β on the basis of these solutions have already been seen to be satisfactory.

Finally, we would like to remark that the sextic double-well potential in conjunction with a short range and weak binding potential can be used to provide an elegant illustration of quantum discontinuities pointed out originally by Calogero (1979). The details of this will be presented elsewhere.

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