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Near the threshold of potentials – quantization rules and scattering lengths

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Abstract. The near-threshold behaviour of the phase loss due to reflection ("the reflection phase") at the outer turning point in an attractive, homogeneous potential tail is obtained analytically up to linear order in energy by adapting the effective-range formalism of scattering theory to the bound state regime. A generalization of the Bohr-Sommerfeld quantization rule based on these results accurately reproduces the eigenenergies close to the threshold. We derive an expression for the reflection phase at arbitrary energy by matching the near-threshold expansion to known formulas for large negative energies. This model, which includes only one free parameter is a significant improvement over the eigenenergies obtained by other approximate methods. Also, the scattering length is completely determined by the knowledge of one of the highest bound energy levels (not necessarily by the highest one) and the asymptotic behavior of the potential.

1. Introduction

Near-threshold properties in atomic and molecular potentials – for energies above or below threshold – are currently in the focus of an intense interest [1–3]. These properties depend mainly on the far tail of the potential, which is often known quite well. In contrast, the short-range part of the potential is generally less well known and often modelled with the help of a few parameters [4]. Properties of near-threshold bound or continuum states can be derived without reference to the short-ranged part of the potential if the distant nodal structure of some near-threshold states is known, either from experiment or from model calculations [5, 6]. In this contribution we present a quantization rule for molecular-type potentials which is based on a generalization of WKB quantization and accurately accounts for the near-threshold energy dependence of the phase loss at the outer classical turning point, the (outer) reflection phase. The present work includes beyond leading-order contributions, both in the low energy near-threshold and in the far-from-threshold regimes, which were not included in previous similar studies [7, 8]. Knowledge of the near-threshold quantization rule allows an immediate determination of the scattering length, which is related to the time delay of an almost monochromatic s-wave packet scattered at near-threshold energies.

2. A quick recollection of WKB-theory

WKB waves (Wentzel, Kramers and Brillouin) provide an accurate approximation of the exact wavefunction in the semiclassical limit of a quantum-mechanical problem defined by the global condition (see, e.g., [9]):

$$S(E) \gg \hbar, \tag{1}$$

with the action:

$$\frac{S(E)}{2} \equiv \int_{r_{\rm in}(E)}^{r_{\rm out}(E)} p(r)\,{\rm d}r \tag{2}$$

and the local classical momentum:

$$p(r) = \sqrt{2M\left[E - U(r)\right]}. \tag{3}$$

In the classically allowed region the WKB wave takes the form:

$$\psi(r) \propto \frac{1}{\sqrt{p(r)}} \cos\left(\frac{1}{\hbar}\left|\int_{r_0}^{r} p(r')\,{\rm d}r'\right| - \frac{\phi}{2}\right), \tag{4}$$

where the reference point r_0 determines the overall phase of the wave. It is customary to choose it to be the classical turning point $r_{\rm ctp}$. The phase ϕ is the reflection phase at the reference point $r_{\rm ctp}$, i.e., the phase loss due to reflection at the classical turning point. In the classically forbidden regions WKB solutions are exponentially decaying functions.

However, the WKB approximation might be good, even when (1) is not fulfilled. In general, WKB waves are a good approximation if the following local condition applies:

$$\hbar^2 \left|\frac{3}{4}\frac{p'^2(r)}{p^4(r)} - \frac{p''(r)}{2p^3(r)}\right| \ll 1. \tag{5}$$

This condition is violated near a classical turning point $r_{\rm ctp}$. The reflection phase ϕ in (4) is defined so that the WKB wave has the correct phase in the classically allowed region away from the classical turning point.

3. Calculating the reflection phase

In this contribution we focus our investigation on homogeneous potential tails, i.e. on potentials which behave as

$$U(r) = -\frac{\hbar^2}{2M}\frac{\beta_\alpha^{\alpha-2}}{r^\alpha},\ \alpha > 2, \tag{6}$$

in the nonclassical region where (5) is not well fulfilled and beyond. For a homogeneous potential (6) the WKB approximation is increasingly accurate for increasing absolute value of the energy $|E|$ (global condition) and, at arbitrary energy, for decreasing value of the coordinate r (local condition).

Adapting the effective-range formalism of scattering theory [10, 11] to the bound state regime yields an expression for the reflection phase up to linear order in energy $E^< = -\hbar^2\kappa^2/(2M) < 0$:

$$\begin{aligned}\phi_{\rm out}^{\ll}(\beta_\alpha\kappa) &= \phi_0 + \frac{1}{\hbar}\left[S_{\rm hom}(E^<) - S_{\rm hom}(0)\right] + 2b\kappa - (d\kappa)^2 \\ &= \frac{\pi}{2} + \nu\pi - \frac{2}{\alpha-2}(\beta_\alpha\kappa)^{1-\frac{2}{\alpha}}\frac{\alpha\sqrt{\pi}\Gamma\left(1-\frac{1}{\alpha}\right)}{\Gamma\left(\frac{1}{2}-\frac{1}{\alpha}\right)}\tan\left(\frac{\pi}{\alpha}\right) + 2b\kappa - (d\kappa)^2\end{aligned} \tag{7}$$

with $\nu = 1/(\alpha-2)$ and

$$\begin{aligned}\frac{b}{\beta_\alpha} &= \frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\nu^{2\nu}\sin(\nu\pi)\,, \\ \left(\frac{d}{\beta_\alpha}\right)^2 &= \frac{2\pi^2\nu^{2\nu+1}}{\Gamma^2(1+\nu)}\left[\frac{(2\nu)^{2\nu}\,\Gamma\left(\frac{1}{2}+2\nu\right)\nu}{\Gamma\left(\frac{1}{2}+\nu\right)\Gamma(1+3\nu)\sin(\nu\pi)} - \frac{1}{\pi}\frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\nu^{2\nu}\cos(\nu\pi)\right].\end{aligned} \tag{8}$$

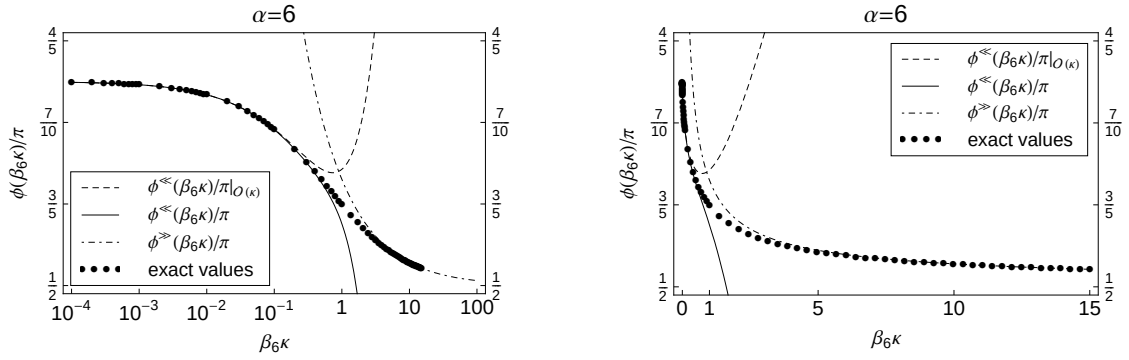

Figure 1. Outer reflection phase for a homogeneous potential (6), $\alpha = 6$, as function of $\kappa\beta_6$. The dots are the numerically calculated exact values. The solid lines show the near-threshold expansion (7) and dashed lines show the results of this expansion when the last term proportional to κ^2 is omitted. The dot-dashed lines show the far-from-threshold expansion (9).

The last term proportional to κ^2 in (7) only exists as given for $\alpha > 3$.

For large negative energies, the behaviour of the reflection phase is [8],

$$\phi_{\text{out}}^{\gg}(\beta_\alpha\kappa) = \frac{\pi}{2} + \frac{D}{(\beta_\alpha\kappa)^{1-\frac{2}{\alpha}}}, \quad D = \frac{\sqrt{\pi}}{12}\frac{\alpha+1}{\alpha}\frac{\Gamma\left(\frac{1}{2}-\frac{1}{\alpha}\right)}{\Gamma\left(1-\frac{1}{\alpha}\right)}. \tag{9}$$

Figure 1 shows the numerically calculated exact outer reflection phase in a homogeneous potential (6) for $\alpha = 6$ (dots) together with the near-threshold expansion (7) (solid lines) and the far-from-threshold expansion (9) (dot-dashed lines). The dashed lines show the near-threshold expansion (7) without the last term proportional to κ^2.

4. Improving WKB quantization

Consider a given potential well with a potential tail falling off faster than $-1/r^2$. For a given negative energy we assume that there exists a semiclassical region (which can be arbitrarily small) between the inner and outer classical turning points, where WKB wave functions are accurate solutions of the Schrödinger equation. The reflection phases ϕ_{in} and ϕ_{out} at the inner and outer turning points can then be defined by the requirement that the WKB wave, e.g. (4), have the right phase in the semiclassical region. The WKB-quantization rule is thus generalized to

$$\frac{S(E_n)}{2\hbar} = \frac{1}{\hbar}\int_{r_{\text{in}}(E_n)}^{r_{\text{out}}(E_n)} p(r)\,\mathrm{d}r = n\pi + \frac{\phi_{\text{in}}}{2} + \frac{\phi_{\text{out}}}{2}, \tag{10}$$

and is in principle exact. In conventional WKB-quantization, the reflection phases are chosen as $\phi = \pi/2$. This is often a good approximation for the inner reflection phase, but conventional WKB quantization breaks down in the anticlassical region near threshold, because the outer reflection phase depends strongly on energy here, see Eq. (7) and Fig. 1. The terms containing the action integrals in (7) actually cancel the leading contribution of the action integrals in the quantization rule (10), so the near-threshold quantization rule assumes a universal form

$$n \overset{E\to 0}{\sim} n_{\text{th}} - \frac{b}{\pi}\kappa_n + \frac{(d\kappa_n)^2}{2\pi}, \tag{11}$$

where n_{th} is the not necessarily integer value obtained from the quantization rule at threshold,

$$n_{\text{th}} \equiv \frac{S(0)}{2\pi\hbar} - \frac{\phi_{\text{out}}(0)}{2\pi} - \frac{\phi_{\text{in}}(0)}{2\pi}. \tag{12}$$

For homogeneous potential tails (6) we can obtain a good approximation for the outer reflection phase at arbitrary energies by interpolating between the known near-threshold and far-from-threshold forms (7) and (9) with the help of an auxiliary function $A(E)$ which is unity at threshold and vanishes for large negative energies:

$$\phi_{\rm out}^{\rm Fit}\left(\beta_\alpha\kappa\right) = A(E)\phi_{\rm out}^{\ll}\left(\beta_\alpha\kappa\right) + \left[1 - A(E)\right]\phi_{\rm out}^{\gg}\left(\beta_\alpha\kappa\right) \ . \tag{13}$$

Since the near-threshold expansion (7) contains terms up to and including $O(E)$, we choose the form of $A(E)$ so that the leading modification of (7) has order E^2,

$$A(E) = \frac{1}{1 + (B\kappa)^4}. \tag{14}$$

The parameter B has the dimension of a length and is determined by fitting the expression (13) to the numerically calculated exact values of the outer reflection phase. Values of B (in units of β_α) are given in Table 1 together with the relative and absolute errors. The maximum deviation of the phase given by (13) from the numerically calculated exact reflection phase is less than 10^{-3} radians for $\alpha = 6$ or 7 and less than 10^{-2} radians for $\alpha = 4$ or 5.

In order to demonstrate how a better consideration of reflection phases improves the accuracy of WKB quantization, we study the bound states in a Lennard-Jones potential,

$$V_{\rm LJ}(r) = \mathcal{E}\left[\left(\frac{r_{\rm min}}{r}\right)^{12} - 2\left(\frac{r_{\rm min}}{r}\right)^{6}\right] = \frac{\hbar^2}{2M}\frac{B_{\rm LJ}}{(r_{\rm min})^2}\left[\left(\frac{r_{\rm min}}{r}\right)^{12} - 2\left(\frac{r_{\rm min}}{r}\right)^{6}\right] \ . \tag{15}$$

The energy eigenvalues in units of the potential depth $\mathcal{E}$ depend only on the dimensionless strength parameter $B_{\rm LJ}$, and there are 24 bound states for $B_{\rm LJ} = 10^4$. The accuracy of the energy eigenvalues obtained with different quantization rules is illustrated in Fig. 2, which shows the relative errors

$$\Delta E_n = \frac{E_{n,\rm Fit} - E_{n,\rm exact}}{E_{n,\rm exact} - E_{n-1,\rm exact}} \ . \tag{16}$$

The squares show the results obtained with conventional WKB quantization, where both reflection phases are taken as $\pi/2$ independent of energy, and the filled circles are the results obtained when the outer reflection phase is given by (13). Appropriate consideration of the outer reflection phase is shown to improve the accuracy of the energy eigenvalues by one or two orders of magnitude and leads to a relative error uniformly near 10^{-4} and even smaller near threshold. The diamonds show the results obtained with a two-parameter fit, which was introduced in [7] to model the behaviour of the outer reflection phase in the near-threshold region. The authors of [7] were not so concerned about the far-from-threshold behaviour of $\phi_{\rm out}$, and their fit does not reproduce the next-to-leading term proportional to $(\beta_\alpha\kappa)^{-(1-2/\alpha)}$ in (9); hence the poorer performance for the lower-lying bound states.

5. Scattering lengths

If we write the quantization rule in the general form

$$n_{\rm th} - n = F(E) \ , \tag{17}$$

then the behaviour of the function $F(E)$ for homogeneous potential tails (6) is given via (10), (12) and (13) as:

$$F(E) = \frac{2b\kappa - (d\kappa)^2}{2\pi[1 + (B\kappa)^4]} + \frac{(B\kappa)^4}{1 + (B\kappa)^4}\left[-\frac{1}{2(\alpha-2)} + \frac{\Gamma\left(\frac{1}{2} + \frac{1}{\alpha}\right)(\kappa\beta_\alpha)^{1-2/\alpha}}{(\alpha-2)\sqrt{\pi}\,\Gamma\left(1 + \frac{1}{\alpha}\right)} + \frac{D}{2\pi(\kappa\beta_\alpha)^{1-2/\alpha}}\right] \ , \tag{18}$$

α	B/β_α	$\max_j\{\Delta_{\rm rel}\phi_j\}$	$\max_j\{\Delta_{\rm abs}\phi_j\}$	b/β_α	d/β_α	D
4	2.3528	0.00730	1	0.00540	$\sqrt{2\pi/3}$	0.54626
5	1.3035	0.00309	0.00167	0.63134	0.70526	0.45544
6	0.93323	0.00040	0.00022	0.47799	0.45795	0.40897
7	0.73446	0.00121	0.00071	0.39151	0.33557	0.38062

Table 1. Parameter B (in units of β_α) obtained by fitting the expression (13) to the numerically values of the outer reflection phase for homogeneous potentials (6), as well as the corresponding absolute and relative errors.

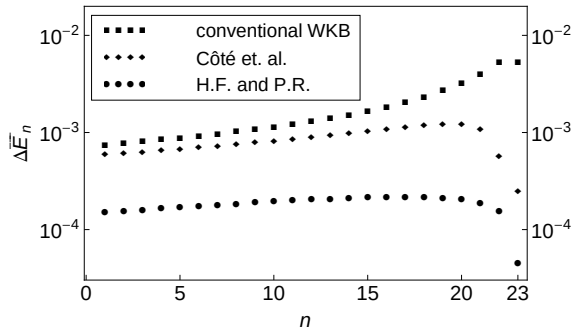

Figure 2. Relative errors (16) for the energy eigenvalues in the Lennard-Jones potential (15) with $B_{\rm LJ} = 10^4$. The squares show the results of conventional WKB quantization with $\phi_{\rm in} = \phi_{\rm out} = \pi/2$; the diamonds show the results obtained when $\phi_{\rm out}$ is given by the two-parameter fit formula of [7], and the filled circles show the results obtained with the one-parameter interpolation formula (13) for $\phi_{\rm out}$.

with b and d as given by (8). The scattering length a is related to the threshold quantum number $n_{\rm th}$ by [9]

$$a = \bar{a} + \frac{b}{\tan(n_{\rm th}\pi)} \ , \tag{19}$$

where $\bar{a}$ is the mean scattering length, which is given by $\bar{a} = b/\tan(\pi\nu)$ for homogeneous potential tails (6). With (11) we can expand a in terms of the inverse penetration depth κ_n of a near-threshold bound state:

$$a \overset{\kappa_n\to 0}{\sim} \frac{1}{\kappa_n} + \bar{a} + \frac{d^2}{2b} + O(\kappa_n) \ . \tag{20}$$

The quantization rule (17) allows a more general expression for the scattering length [12],

$$a = \bar{a} + \frac{b}{\tan[\pi F(E_n)]} \ , \tag{21}$$

where E_n is the energy of a highly excited — not necessarily the most highly excited — state.

The power of equation (21) can be demonstrated with the help of the Lennard-Jones potential (15). We focus on the $n = 23$ state which is the highest bound state for $B_{\rm LJ} = 10^4$. By varying $B_{\rm LJ}$ we vary the energy — and the inverse penetration depth κ_n of the $n = 23$ state in the range from zero to $60/\beta_6$, $\beta_6 = r_{\rm min}(2B_{\rm LJ})^{1/4}$. The corresponding scattering lengths are shown in the left-hand half of Fig. 3 (dots) and compared with the predictions of (21), with $F(E_n)$ as

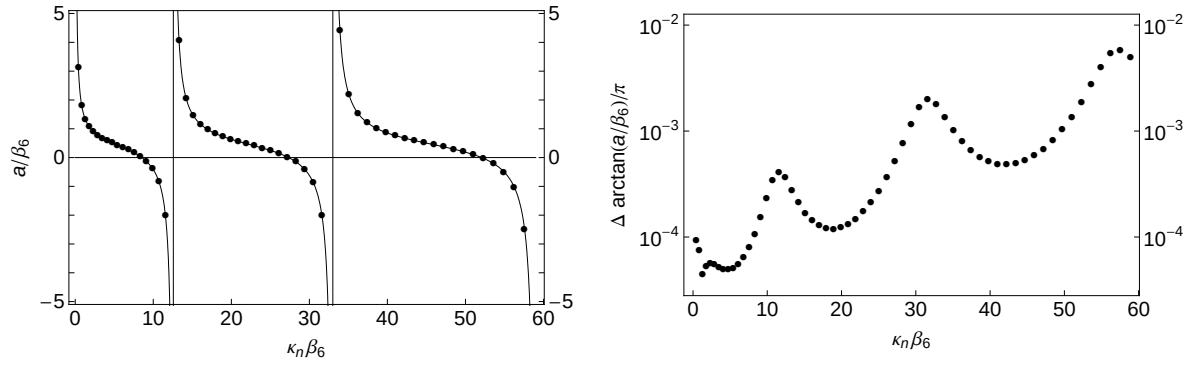

Figure 3. Scattering length for the Lennard-Jones potential (15) for a range of values of the potential parameter $B_{\rm LJ}$. The abscissa is labelled by the product $\kappa_n\beta_6$ of the inverse penetration depth of the $n = 23$ state and the length $\beta_6 = r_{\rm min}(2B_{\rm LJ})^{1/4}$ characterizing the strength of the potential tail. The dots in the left-hand panel are the scattering lengths obtained by numerically solving the Schrödinger equation and the solid lines show the results obtained with the formula (21) with the function $F(E)$ given by (18) and $\alpha = 6$. The right-hand panel illustrates the accuracy in terms of the error in the angle (in units of π) $\arctan(a/\beta_6)$.

given by (18) for $\alpha = 6$ (solid lines). As shown in the right-hand half of the figure, the explicit formula (21) reproduces the correct scattering length with an accuracy at the percent level or better, even when the bound state involved is not the highest state (which is only the case for $\kappa_n\beta_6$ less than about 12).

Calculation of the scattering length builds a bridge to the subject "time", which was the topic of the workshop. According to [13], the time delay of an almost monochromatic wave packet scattered by a potential such as (15) relative to a free particle reflected at $r = 0$ is given by the energy derivative of the (s-wave) scattering phase shift δ via:

$$t_{\rm delay} = \hbar \frac{{\rm d}\delta}{{\rm d}E^{>}}. \tag{22}$$

The near-threshold behaviour of the phase shift is,

$$\delta\left(k\right) \overset{k\to 0}{\sim} n\pi - ka + \mathcal{O}\left(k^3\right), \tag{23}$$

where k is the wave number, $E^{>} = \hbar^2k^2/(2M) > 0$. For small positive energies, $k \to 0$, the time delay of almost monochromatic wave packet is thus given by:

$$t_{\rm delay} = -\frac{aM}{\hbar k}. \tag{24}$$

6. Conclusion and outlook

This work gives an analytical expression of the outer reflection phase in homogeneous potentials up to linear order in energy and by using it one can deduce a new formula for near-threshold quantization and an approximate expression for the scattering length, which determines the time delay of almost monochromatic wave packets near threshold.

Further work will deal with extending the range of examples to more physical potentials, establishing connections to quantum reflection at above threshold energies and with the derivation of new analytical expressions for the near-threshold properties of potentials with nonhomogeneous tails.

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