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Analytical correction to the WKB quantization condition for the highest levels in a molecular potential

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Abstract. We have recently shown that the highest vibrational level in a molecular potential is not well described by the semiclassical JWKB quantization formula and that there is a complete analogy between this effect and the quantum threshold behaviour for continuum levels. The goal of the present paper is to complete the description of this effect. In a first step, we verify that the quantization condition for zero-energy bound states deduced from the work of Gribakin and Flambaum on the scattering length is very accurate. Then, we discuss the correction term to the JWKB quantization condition, using numerical calculations as well as various analytic approximations. In particular, the second order JWKB formula for this phase correction term and a new resonant expression are introduced, and we also improve our previous numerical integral method. The discussion is centered mostly on the case of long range potentials behaving like r^{-6} at long range but the case of a r^{-3} behavior is also considered and most of the formulas developed here are valid for any $n \geq 3$. Finally, we show how to deduce the scattering length from the binding energy of the highest vibrational level.

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1 Introduction

In recent years, there has been a renewed interest in the quantum aspects of atom-atom interactions at very low positive or negative energies. This interest is a directly linked to the numerous experiments using very cold atoms. Moreover, elastic collisions play a very important role in the production of Bose-Einstein condensation and the stability of the condensate depends of the sign of the atom-atom scattering length a. The value of this parameter can be deduced either from the continuum wavefunction at very low energies through photoassociation spectroscopy, or from a very accurate spectroscopy of the highest vibrational levels.

Photoassociation spectroscopy can be used to probe of the highest vibrational levels very close to an excited dissociation limit [1–4]. A refined analysis of molecular potentials in the range of large internuclear distances can thus be achieved and very accurate informations on the long range interactions between two neutral atoms can be derived. The photoassociation spectrum permits also to deduce the nodal structure of the continuum wavefunction describing the relative motion of two atoms in their ground state [5,6] and from this information, precise values of the scattering length have been deduced [7,8]. A very accurate spectroscopy of the highest vibrational levels of the molecular states connected to the lowest atomic limit can be achieved in various cases and this information can also be used to deduce the values of the scattering length (for example see Ref. [9]).

Levinson's theorem [10,11] proves that the magnitude and sign of the scattering length a is directly connected to the position of the highest vibrational level in the ground molecular potential. For almost all molecular potentials, there are several and usually many vibrational levels. Although the highest vibrational level is always very close to the dissociation limit with respect to the usual scale of molecular energies, its distance to the dissociation limit can be in a range extending from zero to a maximum value which depends only on a few parameters (the C_n coefficient of the dominant long range term $-C_n/r^n$ of the potential, the reduced mass μ of the two atoms and $\hbar$). If we imagine that we can tune the value of the reduced mass μ, the number of bound levels increases with the reduced mass and the scattering length varies in a quasi-periodic fashion: it is infinite and positive when a new level has just entered in the potential, then it decreases in a monotonic

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fashion and finally becomes infinite and negative just before the appearance of the next level. Therefore, it is important to understand in detail the position of the highest vibrational level. All the discussion of the present paper assumes a single channel problem, whereas most cases of experimental relevance are multichannel problems. Therefore, our discussion applies to the experimental cases only if their multichannel character is negligible. We feel however that an understanding as complete as possible of the single channel problem is a prerequisite for the understanding of the general problem.

In our previous letter [12], we have shown that the JWKB quantization condition fails for the highest vibrational levels in a molecular potential. Our starting point was the remark that the quantization condition for a zero energy bound state [11] differs from the standard JWKB quantization condition. To fill the gap between these two limiting cases, we have introduced a correction term ε in the standard JWKB quantization condition and we have investigated numerically this correction term. We have also studied the special properties of the highest vibrational levels, in particular the fact that the probability of presence can be totally in the classically forbidden region at large distances. All these results were interpreted as a mirror effect for bound states of the quantum threshold regime for the continuum states. Our work was commented by Trost *et al.* [13], who had previously established several analytic results concerning Maslov indices [14–17]. The present paper completes our previous analysis of the problem, including new analytic approximate formulae for the correction term ε and a larger set of numerical tests of the analytic results.

In Section 2, we recall the previous analytical results concerning the vibrational levels in a Lennard Jones 12-6 molecular potential. We first present numerical tests of the Gribakin and Flambaum [11] analytic formula giving the scattering length as a function of the potential parameters and of the reduced mass. From the observed divergence of the scattering length, we deduce very accurate values of the quantum parameter for potential curves holding a zero-energy state. We compare these results to previous knowledge, thus showing the need for an improved analysis. In Section 3, we present further numerical tests of the Leroy Bernstein and Stwalley [19–21] semiclassical quantization condition for vibrational levels very close to the dissociation limit in the cases of potentials presenting a r^{-6} and a r^{-3} long-range behavior. We thus verify that the correction term of this quantization condition for the highest levels has a universal character, depending only of the long-range dominant term of the potential. We then discuss various approximations of this correction term, including an improved form of our previous results [12], the calculation of Trost, Eltschka and Friedrich [17] and a JWKB approximation. Finally, we explain how to evaluate the scattering length using as input the binding energy of the highest vibrational level and the long range (C_n) parameter of the potential. This method is successfully tested in several cases corresponding to r^{-6} potentials. A few concluding remarks end the paper.

2 Quantization condition of bound states in a molecular potential

2.1 Schrödinger equation and numerical techniques

The wavefunctions and the energies of the rotationless vibrational levels are obtained by solving the single channel Schrödinger equation:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\Psi}{\mathrm{d}r^2}+V(r)\Psi=E(v)\Psi \tag{1}$$

where r is the internuclear distance and $V(r)$ is the interatomic potential. We assume that $V(r)$ is repulsive at short range, attractive at long range and that it behaves like $-C_n/r^n$ when r goes to infinity. A common general form used here will be Lennard-Jones potentials of the type:

$$V(r)=\frac{C_m}{r^m}-\frac{C_n}{r^n}=\left[\left(\frac{\sigma}{r}\right)^{m-n}-1\right]\frac{C_n}{r^n} \tag{2}$$

where σ is the hard core radius and $m>n$. Most calculations will use 12-6 Lennard-Jones potentials given by:

$$V(r)=4D_\mathrm{e}\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

where D_e is the well depth and the equilibrium distance r_e is given by $r_\mathrm{e}=2^{1/6}\sigma$. The dominant long-range term is $-C_6/r^6$, with the C_6 coefficient given by $C_6=4D_\mathrm{e}\sigma^6$. If one uses D_e as the energy unit and σ as the length unit, the Schrödinger equation can be given a dimensionless form which depends of only one "quantum" parameter given by [22] (another common form of the quantum parameter is obtained by replacing r_e by σ in the following equation):

$$B=\frac{2\mu D_\mathrm{e} r_\mathrm{e}^2}{\hbar^2}\,\cdot \tag{4}$$

Standard numerical resolutions of the Schrödinger equation use a grid of points to propagate the solution with a fixed step interval h. In the case of bound or continuum levels very close to the dissociation limit, these methods present some disadvantages. To insure convergence [23], a small h value is needed at short internuclear distances where the wavevector $k(r)$ is large, while a considerably larger value of h should be used at large internuclear distances where the local wavevector is extremely small. If one uses everywhere a small h value, the resulting number of points in the grid used for the calculation becomes extremely large and the computation becomes very time-consuming. To avoid these problems, we have developed a dedicated computer program. This program uses the common 3-point Numerov algorithm which is valid up to 5th order in the step h. Following the procedure first developed by Blatt [23] and recently used by Côté and Jamieson [24] for the study of ultra-cold atom collisions, the value of h is doubled or divided by 2 whenever necessary so as to keep the product $k(r)h$ close to the value 10^{-3} which we have found to be optimum with the present Numerov algorithm. Our code can be used for continuum levels and it then provides the s-wave phase shift. In the case of discrete states, it includes a modified form of the level seeking method due to Cooley and Cashion [25,26], adapted to the case of a variable step size and to the specific properties of bound states very close to the dissociation limit. We have thus been able to calculate efficiently and accurately the energies of the highest bound states and the associated wavefunctions even when the wavefunction is non negligible in an unusually large range of internuclear distances (typically $10^5 a_0$) and when the binding energy is extremely small. With r^{-6} potentials, we have worked down to energies of the order of 10^{-15} a.u. and outer turning points near $3\,000 a_0$ and with r^{-3} potentials we have even reached energies as small as 10^{-21} a.u. and outer turning points as large as $10^6 a_0$.

2.2 First order JWKB quantization condition: Leroy Bernstein and Stwalley near dissociation expansion (NDE)

The common semiclassical treatment used to describe the series of vibrational levels converging towards the dissociation limit was independently derived by LeRoy and Bernstein [19,20] and by Stwalley [21] in 1970. The energy $E(v)$ of the vibrational level v is implicitly given by the first order JWKB quantization condition:

$$\Phi(E(v)) = \left(v + \frac{1}{2}\right)\pi \tag{5}$$

with the phase integral $\Phi(E(v))$ given by:

$$\Phi(E(v)) = \frac{1}{\hbar}\int_{r_1}^{r_2} p(r)\,\mathrm{d}r. \tag{6}$$

Here $p(r)$ is the local momentum:

$$p(r) = \sqrt{2\mu(E(v) - V(r))} = \hbar k(r)$$

and $k(r)$ is the local wavevector. The inner and outer turning points of the classical motion are labeled r_1 and r_2: $V(r_1) = V(r_2) = E(v)$. If the potential is well represented at large internuclear distances by the leading term of its electrostatic expansion $V(r) = -C_n/r^n$ with $n \geq 3$ (the rest of the potential is not specified but a repulsive wing at short range is assumed), then following LeRoy, Bernstein [19,20] and Stwalley [21], the energy $E(v)$ is a simple function of v:

$$E(v) = -\left[H_n(v_\mathrm{D} - v)\right]^{\frac{2n}{n-2}}. \tag{7}$$

Let us recall that our energy zero is the dissociation energy and H_n is given by:

$$H_n = \hbar\frac{\Gamma(1+1/n)}{\Gamma(1/2+1/n)}\sqrt{\frac{\pi}{2\mu}}\frac{(n-2)}{C_n^{1/n}} \tag{8}$$

where $\Gamma(x)$ is the gamma function. An interesting remark is that the quantity $(H_n)^{\frac{2n}{n-2}}$, is the only combination of $\hbar$, μ and C_n which has the dimension of an energy. Therefore, it is very close, within a factor of the order of unity, to the energy width of the quantum threshold region as estimated by Julienne and Mies [27]. Finally, the effective non integer vibrational quantum number at the dissociation limit v_D is related to the phase integral Φ_D calculated for the dissociation energy:

$$\Phi_\mathrm{D} = \Phi(E=0) = \left(v_\mathrm{D} + \frac{1}{2}\right)\pi. \tag{9}$$

This description of the vibrational levels close to the dissociation limit revealed to be extremely successful to represent experimental data. However, in 1980, Kirschner and LeRoy [28,29] using numerical calculations proved that this formula failed for the highest level. They also observed that the introduction of several higher order JWKB terms was not sufficient to correct uniformly this discrepancy. A similar result was established by Pan and Mies for high-n Rydberg levels [30].

2.3 Gribakin and Flambaum formula for the scattering length

The wavefunction for zero energy (*i.e.* the energy of the dissociation limit) has been studied in an early work by Berry and Mount [31] in the case of potential without a repulsive core and more recently by Gribakin and Flambaum [11] in various cases relevant to molecular physics. These authors have derived an analytical expression of the scattering length a defined as usual by:

$$a = -\lim_{k\to 0}\frac{\tan(\delta_0)}{k} \tag{10}$$

where δ_0 is the s-wave phaseshift and k the wavevector when r goes to infinity. In the range where the potential is well approximated by the long range $-C_n/r^n$ term, there is a classic analytical expression of the zero energy wavefunction for the s-wave ($l = 0$). By matching this expression to the JWKB wavefunction in a region where this approximation is valid, Gribakin and Flambaum deduced the following analytical expression of a:

$$a = \bar{a} - \bar{a}\tan\left(\frac{\pi}{n-2}\right)\tan\left(\Phi_\mathrm{D} - \frac{\pi}{2(n-2)}\right) \tag{11}$$

with

$$\bar{a} = \cos\left(\frac{\pi}{n-2}\right)\left(\frac{\sqrt{2\mu C_n}}{\hbar(n-2)}\right)^{\frac{2}{n-2}}\frac{\Gamma\left(\frac{n-3}{n-2}\right)}{\Gamma\left(\frac{n-1}{n-2}\right)}\cdot \tag{12}$$

This formula and the JWKB quantization condition are contradictory: this remark was the starting point of our previous paper [12]. Following Levinson's theorem [10], an infinite scattering length is associated to a zero energy bound state and equation (11) predicts that such a state exists when:

$$\Phi_{\rm D} = \left(v_{\max} + \frac{1}{2} + \frac{1}{2(n-2)} \right) \pi \tag{13}$$

where $v_{\max}$ is the integer which labels the highest vibrational level. The near dissociation expansion (NDE) result predicts a zero energy bound state if:

$$\Phi_{\rm D} = \left(v_{\max} + \frac{1}{2} \right) \pi. \tag{14}$$

Therefore, equation (13) predicts a zero energy bound state each time that $v_{\rm D} = v_{\max} + \frac{1}{2(n-2)}$, while in the NDE formalism (Eq. (14)), a zero energy bound state occurs each time that $v_{\rm D}$ is an integer (then $v_{\rm D} = v_{\max}$). In our previous work [12], we have introduced a phase correction term ε

$$\Phi(E(v)) = \left(v + \frac{1}{2} + \varepsilon \right) \pi. \tag{15}$$

Depending of the value of ε, this formula can interpolate between the two regimes. The variations of ε are discussed in Section 3. We are first going to evaluate the accuracy of the quantization condition for zero-energy bound states (formula (13)) deduced from the work of Gribakin and Flambaum.

2.4 Numerical test of the Gribakin and Flambaum formula and number of bound states in a Lennard Jones 12-6 potential

It is interesting to make numerical tests of this analytic result, especially because the question of the number of bound states in analytic potentials has received much attention. For these tests, we have used Lennard-Jones 12-6 potentials for which $\Phi_{\rm D}$ is related to the quantum parameter B (Eq. (4)) by an analytic expression:

$$\Phi_{\rm D} = \frac{\sqrt{2\pi\mu C_6}}{12\hbar\sigma^2} \frac{\Gamma(1/3)}{\Gamma(11/6)} = 0.23858\pi\sqrt{B}. \tag{16}$$

For the calculations, we have used the sodium dimer reduced mass ($\mu = 11.49488385$ a.m.u.) and we have varied the well depth $D_{\rm e}$, while keeping the hard core radius σ constant ($\sigma = 8.06a_0$). In Figure 1, we compare the predictions of the analytic expression (11) giving the scattering length with numerical estimates. When the potential is deep enough to hold many bound states, the agreement is truly excellent, the relative difference between the two results being close to 10^{-3}. From various convergence tests, we have estimated the relative error of our numerical calculation of the scattering length to be better than 10^{-6}, if we except the neighborhood of the points where a vanishes or diverges. The agreement is obviously less good in these regions. For shallow potentials holding only a few vibrational levels, the general agreement between the two calculations remains as good, but there is a clear shift between the $D_{\rm e}$ values for which the scattering length diverges. We have determined the $D_{\rm e}$ values corresponding to an infinite scattering length and calculated the corresponding critical values $B_{\rm c}$ of the quantum parameter. These results can be compared to several works devoted to the question of the number N of bound states in various types of analytical potentials including 12-6 Lennard-Jones potentials (for a brief review, see Pauly [22]). We are going to discuss several analytical approximations of the number N as a function of the critical values $B_{\rm c}$ of the quantum parameter. Using the first order JWKB approximation including the Gribakin and Flambaum correction, we obtain a first approximation N_1 by using equation (13) relating $\Phi_{\rm D}$ to $v_{\max} = N_1 - 1$ and the analytical expression of $\Phi_{\rm D}$ (Eq. (16)):

$$N_1 - 1 = c_1\sqrt{B_{\rm c}} - c_2 \tag{17}$$

with $c_1 = 0.23858$ and $c_2 = 0.625$. Values of c_1 and c_2 from various origins are collected in Table 1. It is interesting to remark that Pauly, using numerical results already found $c_2 = 0.6302$ in reasonably good agreement with the theoretical value $c_2 = 0.625$ while a pure first order JWKB

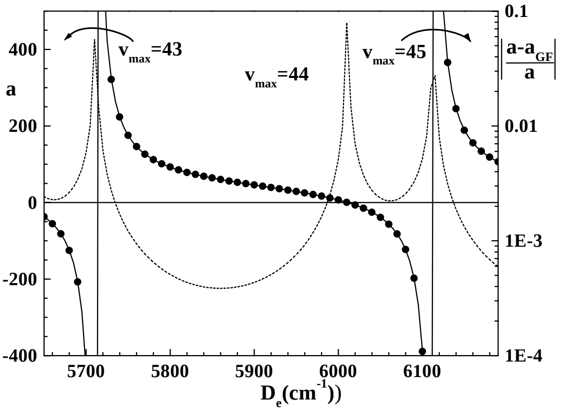


Fig. 1. Comparison of the scattering length (left scale) calculated either numerically (line) or using the analytical formula of Gribakin and Flambaum (points). The dashed line (right scale) is the relative difference between the two results which stays below 10^{-3} except when a is close to zero or when a diverges.

Table 1. Values of the coefficients of the development of the number N of bound states held in a LJ(12, 6) potential in terms of the power of the square root of the critical parameter $B_{\rm c}$. Fit 1 is due to Pauly [16]. Fit 2 is obtained in the same way with our numerical data set. For these two fits, the coefficient c_3 has been fixed to 0. For fit 3, we have fixed the value of c_1 to the value obtained in fit 2 and we have fitted c_2 and c_3. The values obtained in this last fit are remarkably close to the theoretical ones listed in the last column.

	fit 1	fit2	fit 3	theory
c_1	0.2397	0.23866(2)	0.23866	0.23858
c_2	0.6302	0.6292(8)	0.62504(2)	0.625
c_3	/	/	−0.0258(7)	−0.027281

approximation gives $c_2 = 0.5$. We have made a similar fit (see Tab. 1) in very good agreement with the one of Pauly, although the two data sets should be different. We have investigated the quality of our fit by plotting the quantity $\Delta N = N - N_1$ with c_1 and c_2 fixed to their theoretical values as a function of N (see Fig. 2). The deviation is small and decreases rapidly with N. To explain this deviation, we have modified equation (13) to include the second order term of the JWKB expansion. For a zero energy level, this term can be written [28,32]:

$$\Phi_\mathrm{D} + \frac{\hbar}{48\sqrt{2\mu}} \oint \frac{\mathrm{d}^2 V}{\mathrm{d}r^2} \left(-V(r)\right)^{-3/2} \mathrm{d}r = \left(v_\mathrm{max} + \frac{1}{2} + \frac{1}{2(n-2)}\right)\pi. \quad (18)$$

The contour integral appearing in the second order JWKB term is in the complex plane and the integration must go around the part of the real axis between the two classical turning points (r_1 and r_2, equal here to σ and $+\infty$). The convergence of these integrals is not obvious even when the two turning points are at finite distances [33]. Using a procedure similar to the one of Kirschner and LeRoy [28, 29], this term can be written in closed form for any $2n-n$ Lennard Jones potential [34] and we give here the result for $n = 6$. We thus obtain a second order approximation N_2 of the number of bound states as a function of the quantum parameter:

$$N_2 - 1 = c_1\sqrt{B_\mathrm{c}} - c_2 + \frac{c_3}{\sqrt{B_\mathrm{c}}} \quad (19)$$

with

$$c_3 = -\frac{17 \times 2^{1/6}\Gamma(2/3)}{96\sqrt{\pi}\Gamma(1/6)} = -0.02728. \quad (20)$$

We show in Figure 2 that, if we except the point corresponding to $N = 1$ for which higher order terms of the JWKB expansion are probably non negligible, $\Delta N = N - N_1$ is very well represented by the new term $N_2 - N_1 = c_3/\sqrt{B_\mathrm{c}}$. The theoretical c_3 value compares very well to the one obtained by a numerical fit $c_3 = -0.0258(7)$ (see Tab. 1). An interesting and difficult question is the coherence of this treatment, as the 0.125 correction introduced in the ordinary JWKB quantization condition (13) is already a correction due to a failure of the first-order JWKB approximation. A partial answer comes from the remark that the second order JWKB term scales like $1/\sqrt{B}$ whereas the quantum effect at the dissociation limit is independent of the value of the quantum parameter B and this remark strongly suggests that the two corrections correspond to different physical effects.

As a conclusion, we have verified that the quantization condition deduced from the Gribakhin and Flambaum scattering length formula is in very good agreement with numerical results. Moreover, by adding to this equation the second order JWKB term, we have established an accurate equation predicting the number of bound states in a Lennard-Jones 12-6 potential. This correction will be important especially when the potential does not hold many bound states (typically less than 10). This work can be easily generalized to other analytical potentials, even if, in most cases, the c_1, c_2 and c_3 coefficients cannot be evaluated analytically. Indeed, in equation (19), the terms $c_1\sqrt{B_\mathrm{c}}$ and $c_3/\sqrt{B_\mathrm{c}}$ come from the first and second order JWKB integrals, for which numerical integration can be carried [30]. Finally, the c_2 coefficient which depends only on the long range part of the potential is directly taken from reference [11].

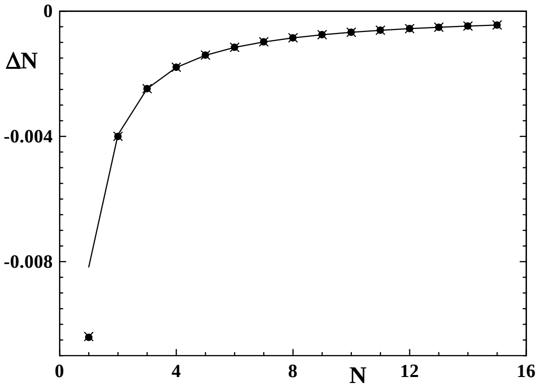


Fig. 2. The full line is a plot of the difference $\Delta N = N - N_1$ between the number N of bound levels of a Lennard-Jones $(12, 6)$ potential and the corrected first order JWKB prediction given by $N_1 - 1 = c_1\sqrt{B_\mathrm{c}} - c_2$ with $c_1 = 0.23858$ and $c_2 = 0.625$. The points represent the theoretical values of the second order JWKB term $N_2 - N_1 = c_3/\sqrt{B_\mathrm{c}}$ with c_3 fixed at its theoretical value $c_3 = -0.02728$ while the crosses represents the values obtained for this term by fitting c_3 to the calculated data, $c_3 = -0.0258(7)$.

3 Corrected quantization condition for the highest vibrational levels

3.1 Numerical tests of the JWKB quantization near the dissociation limit: behavior of correction term ε for n = 6 and n = 3

For the following calculations with $n = 6$, we have used a series of Lennard-Jones 12-6 potential curves which are representative of the ground states of the Li_2, Na_2 and Cs_2 molecules. In each case, the long range C_6 coefficients was fixed while the hard core radius σ and the well-depth D_e were varied. The values of these parameters are given in Table 2. Using about 100 different potentials for each atomic species, we have sampled a large set of cases, covering the complete range of distance from the highest level to the dissociation limit. We calculate in a first step the eigenstate energies $E(v)$ and in a second step the phase integral $\Phi(E(v))$ from which the ε value is easily deduced. In our previous paper [12], the correction term ε was plotted as a function of the quantity $\Phi_\mathrm{D} - \Phi(E_v)$. Because of the strong correlation between ε and $\Phi_\mathrm{D} - \Phi(E_v)$, this choice

Table 2. In this table we collect the values of the parameters used for the calculations of ε. In the first part of the table are reported the parameters depending only of the atomic species. In the second part, we have given the extreme values of the parameters of the LJ(12-6) potentials for $n = 6$ and LJ(6-3) for $n = 3$. We have also indicated the corresponding values of r_2, $\frac{\Phi(E(v_{\max}))}{\pi}$, $E(v_{\max})$, $\alpha_{\rm D}$ and ε.

	Cs ($n = 6$)		Na ($n = 6$)		Li ($n = 6$)		Li ($n = 3$)	
μ (a.m.u.)	66.4527145		11.49488385		3.5080015		3.5080015	
C_n (a.u.)	6329.95		1500		1393.39		11	
$v_{\max}$	114		43		10		61	
	$D_{\rm e\,min}$	$D_{\rm e\,max}$	$D_{\rm e\,min}$	$D_{\rm e\,max}$	$D_{\rm e\,min}$	$D_{\rm e\,max}$	$D_{\rm e\,min}$	$D_{\rm e\,max}$
$D_{\rm e}$ (cm^{-1})	3628.12	3723.9	5711.108	6112.894	507.88	665.1115	324.105	355
σ (a.u.)	6.763536	6.734227	4.933054	4.877472	7.293556	6.972959	12.30298	11.9352
r_2 (a.u.)	3219	85.1	2135	38.29	726.6	27.95	0.31×10^8	0.375×10^5
$\frac{\Phi(E(v_{\max}))}{\pi}$	114.6243	114.512	43.6248	43.512	10.6241	10.5124	61.9522	61.5662
$E(v_{\max})$ (cm^{-1})	0.124×10^{-11}	0.36×10^{-2}	0.34×10^{-11}	0.1044	0.207×10^{-8}	0.6412	0.794×10^{-16}	0.459×10^{-7}
$\alpha_{\rm D}$	0.56×10^{-4}	0.99999	0.58×10^{-4}	0.99999	0.44×10^{-3}	0.99999	0.55×10^{-3}	0.94857
ε	0.1243	0.0119	0.1248	0.0119	0.1241	0.0124	0.4522	0.0662

revealed rather clumsy and the discussion is clarified by introducing a new variable $\alpha_{\rm D}$ defined by:

$$\alpha_{\rm D} = \frac{\Phi_{\rm D}}{\pi} - \frac{1}{2} - \frac{1}{2(n-2)} - v \qquad (21)$$

$\alpha_{\rm D}$, which can be written as $v_{\rm D} - v - \frac{1}{2(n-2)}$, is independent of the total number of bound levels supported by the potential. Equation (13) shows that there is a zero energy bound state when $v_{\rm D}$ is equal to an integer number plus the quantity $\frac{1}{2(n-2)}$ (see Sect. 2.3). Therefore, the quantity $\alpha_{\rm D}$ varies from 0 to 1 for the last bound level, from 1 to 2 for the penultimate one and so on. We have plotted the values of ε as a function of $\alpha_{\rm D}$ in Figure 3. These results correspond to potentials having a r^{-6} long-range asymptotic behaviour and the points corresponding to the three cases are clearly on the same curve. This is a numerical proof that the shape of ε *versus* $\alpha_{\rm D}$ curve is independent of the C_6 value. This independence will be confirmed by the derivation of analytic approximate formulae for ε in the following section. A simple argument can explain this property: in the long range region, where the potential curve is well represented by its long range term $-C_n/r^n$, the Schrödinger equation depends only on $\hbar$, μ and C_n. With these three quantities, one can make one quantity having the dimension of an energy and one quantity having the dimension of a length. Using these quantities as the units of energy and length, the Schrödinger equation takes a unique form at large internuclear distances, and the only adjustable parameter left at a given energy is the phase (rigorously one should speak of the logarithmic derivative) of the wavefunction when entering the long range region. This phase depends sensitively of the inner part of the potential which depends on other parameters than C_n.

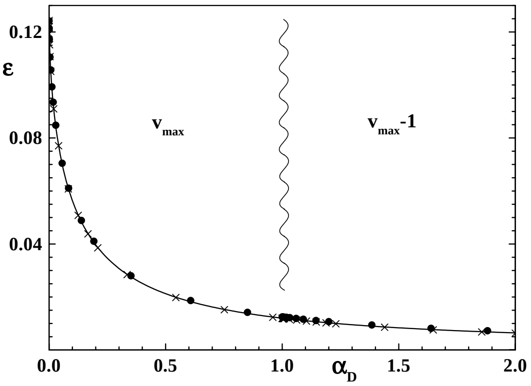


Fig. 3. Variations of the phase correction term ε with the quantity $\alpha_{\rm D}$. The full line interpolates the results obtained in the sodium case, while the full points represent the results obtained in the lithium case (only 1 point over 8 has been plotted) and the crosses represent the results obtained in for the cesium case (only 1 point over 4 has been plotted). Obviously, the variations of ε with $\alpha_{\rm D}$ are extremely similar in these three cases and they do not exhibit any sensitivity to the values of μ or C_6.

In Table 2, we present the calculated ε values in the limiting cases *i.e.* $\alpha_{\rm D} \gtrsim 0$ (the highest level is very close to the dissociation limit corresponding to a large and positive value of the scattering length) and $\alpha_{\rm D} \lesssim 1$ (the highest level is as far as possible from the dissociation limit corresponding to a large and negative value of the scattering length). In the case $n = 6$, the largest values of ε are very close to 1/8 predicted for a zero energy bound state [11]. The very small difference (less than 0.001) between this theoretical value and the numerical result can be explained by slight numerical problems and also by the second order JWKB term discussed above (Sect. 2.4) and neglected here.

The same calculations have been carried out for Lennard-Jones (6-3) potentials with a long range term $-C_3/r^3$, as encountered in the resonance dipole-dipole interaction between two identical atoms when relativistic retardation effects are neglected. The maximum value of the phase correction term ε is then considerably larger, equal to 1/2, but the density of states is also considerably larger and the highest vibrational levels are closer to the dissociation limit. In our calculations, we have tried to minimize the numerical problems by using shallow potentials and a small reduced mass (the one of lithium dimer, see Tab. 2). The highest ε value obtained is $\varepsilon \approx 0.452$, rather far from the maximum theoretical value 0.5. The associated value of the binding energy, below 10^{-16} cm^{-1}, illustrates the difficulty of the numerical calculation.

We will not present a plot of the wavefunctions of the highest vibrational level, as this was done in our previous work [12]. Their shape depends very much of the value of $\alpha_{\rm D}$: if $\alpha_{\rm D}$ is small, the scattering length is large and positive and the corresponding wavefunction is comparable to the continuum wavefunction at very low energies, *i.e.* the inner part presents rapid oscillations, with the number of nodes and their positions almost independent of the exact energy of the level, while the long range part is a very slowly decreasing exponential. The probability of presence in such a state is mostly at long range, and in the limit $\alpha_{\rm D} \to 0$, the probability of presence is totally in the range of internuclear distances greater than the classical outer turning point [12]. It is important to notice here that the position of the last outer node of the wavefunction of the highest bound state (and the corresponding node of the continuum wavefunction at very low energy) is strongly linked [6,7] to the value of the scattering length *i.e.* to the value of $\alpha_{\rm D}$.

The existence of the correction term ε makes that the formula of LeRoy and Bernstein (Eq. (7)) giving the energy of the vibrational levels must be modified. With the present notations, the corrected formula relates the vibrational energy $E(v)$ to the quantities $\alpha_{\rm D}$, ε:

$$E(v) = -\left[H_n\left(\alpha_{\rm D} + \frac{1}{2(n-2)} - \varepsilon\right)\right]^{\frac{2n}{n-2}} \tag{22}$$

with H_n defined by equation (8). Obviously, this modification induces only very small corrections of the energies of the vibrational levels because H_n is usually quite small. But this effect is more important in the other way, if one wants to deduce $\Phi_{\rm D}$ or $\alpha_{\rm D}$ from the binding energies.

3.2 Second order JWKB approximation of the correction term ε

As mentioned above, the deviation from the first order JWKB quantization condition for the highest vibrational levels was first pointed out by LeRoy *et al.* [28,29]. These authors have taken into account several higher order JWKB terms, but with our notations, if $\alpha_{\rm D}$ is very small, the convergence of the JWKB series for the last level is extremely slow and in practice cannot be obtained. We will limit here our discussion to the second-order JWKB term. Then, the phase correction is simply given by:

$$\varepsilon_{\rm WKB2} = -\frac{\hbar}{48\pi\sqrt{2\mu}}\oint \frac{{\rm d}^2V}{{\rm d}r^2}\left(E - V(r)\right)^{-3/2}\,{\rm d}r. \tag{23}$$

The phase correction depends of the energy E of the level. Using the same approximations as in the Near Dissociation Expansion, we can calculate this integral:

$$\varepsilon_{\rm WKB2} = -\frac{\hbar(n+1)}{24n\sqrt{2\pi\mu}}C_n^{-1/n}\left(-E\right)^{\frac{2-n}{2n}}\frac{\Gamma\left(\frac{1}{2}-\frac{1}{n}\right)}{\Gamma\left(1-\frac{1}{n}\right)}\cdot \tag{24}$$

Introducing this correction in equation (22) giving the energy of the vibrational level, we get after a few manipulations:

$$\varepsilon_{\rm WKB2} =$$

$$\frac{(n+1)}{24\pi(n-2)}\tan\left(\frac{\pi}{n}\right)\left(\alpha_{\rm D} + \frac{1}{2(n-2)} - \varepsilon_{\rm WKB2}\right)^{-1}. \tag{25}$$

This is an equation in $\varepsilon_{\rm WKB2}$, with the following relevant solution:

$$\varepsilon_{\rm WKB2} = \frac{1}{4(n-2)} + \frac{1}{2}\alpha_{\rm D}$$

$$-\frac{1}{2}\sqrt{\left(\alpha_{\rm D} + \frac{1}{2(n-2)}\right)^2 - \frac{(n+1)}{6\pi(n-2)}\tan\left(\frac{\pi}{n}\right)}\cdot \tag{26}$$

We have plotted in Figures 4a and 4b this approximation $\varepsilon_{\rm WKB2}$ of the phase correction in the cases $n = 6$ and $n = 3$. The agreement with the numerical estimates of the phase correction ε is excellent for $\alpha_{\rm D}$ values greater than 0.4. In the case $n = 6$, we have calculated numerically the integral (23) and we have found that the result is very close to the analytic result based on the Near Dissociation Expansion approximations in the range $\alpha_{\rm D} \gtrsim 0.4$ where this result is interesting (or $E_{\rm b} \gtrsim 0.1H_n^{\frac{2n}{n-2}}$).

3.3 Formulation of ε in the resonance formalism

If the highest bound level is very close to the dissociation limit, the scattering length becomes very large, and there is a classic relation between the binding energy of the level and the scattering length. Writing the binding energy $E(v_{\rm max}) = -\hbar^2\kappa^2/(2\mu)$, we thus define κ and the resonant part of the s-wave phase shift δ_0 [11,35]:

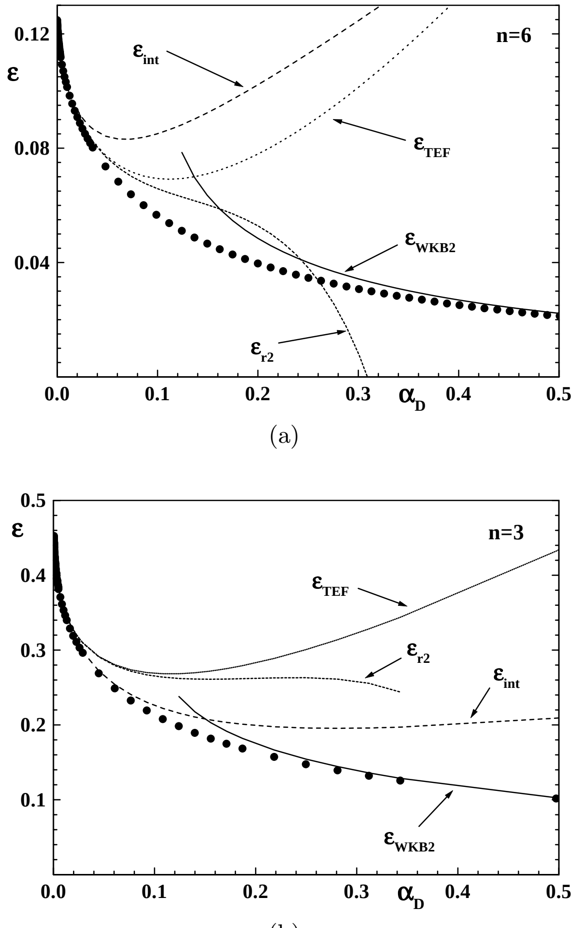
$$\tan\delta_0 = -\frac{k}{\kappa}\cdot \tag{27}$$

Therefore, κ is just the inverse of the scattering length a and, using equations (10, 11, 22), a first analytical approximation of ε labeled ε_{r1} is derived:

$$\varepsilon_{r1} = \frac{1}{2(n-2)} + \alpha_{\rm D} - A\left[1 + \frac{1}{\tan(\pi\alpha_{\rm D})}\right]^{\frac{2-n}{n}} \tag{28}$$

with:

$$A = \frac{1}{\sqrt{\pi}}\frac{\Gamma(\frac{1}{2}+\frac{1}{n})}{\Gamma(1+\frac{1}{n})}\left[\frac{\Gamma(\frac{n-1}{n-2})^2}{\pi}\right]^{\frac{n-2}{n}}\cdot \tag{29}$$



(a)

(b)

Fig. 4. Comparison of the different formulae used in this paper to represent the correction term ε in the case of $n = 6$ (a) and $n = 3$ (b). The points are the numerical values obtained in the sodium case ($n = 6$) and in the lithium case ($n = 3$). The full line is the second order analytical formula (NDE, Eq. (26)). The dashed line is the resonant approximation developed in this paper (Eq. (31)) while the dotted line is the Trost, Eltshka and Friedrich formula (Eq. (32)). Finally, the long dashed line is the numerical integral formula developed at the end of Section 3.3. In the two cases $n = 6$ and $n = 3$, there is a range of α_D values where none of the approximate formulae is accurate.

However it is possible to improve this derivation, by observing that a non resonant part also exists in a. Introducing a non resonant part c in equation (27), we get:

$$\tan\delta_0 = (-c - 1/\kappa)\,k \tag{30}$$

corresponding to $a = -c - 1/\kappa$. Identification with equation (11) suggests that the non resonant part c is equal to $\bar{a}$. We thus get a second analytic expression of ε labeled ε_{r2}:

$$\varepsilon_{r2} = \frac{1}{2(n-2)} + \alpha_D - A\left[\tan(\pi\alpha_D)\right]^{\frac{n-2}{n}}. \tag{31}$$

This expression is valid for small α_D values, typically $\alpha_D \lesssim 0.05$ (or $E_b \lesssim 0.001 H_n^{\frac{2n}{n-2}}$) for $n = 6$ and $\alpha_D \leq 0.1$ (or $E_b \lesssim 0.005 H_n^{\frac{2n}{n-2}}$) for $n = 3$ (see Figs. 4a and 4b).

These analytic approximations of ε *versus* α_D are independent of the long range parameter C_n value and of the reduced mass μ and depend only on the exponent n characteristic of the long range behavior of the potential. We have already discussed this universal character of ε. It is interesting to compare the present result with the calculations of Trost, Eltschka and Friedrich using the formalism of Maslov indices [17,18,36] and phase loss calculations near the classical outer turning point [14–16]. They have derived an analytic formula [13] giving ε which, with the present notations, becomes:

$$\varepsilon_{\text{TEF}} = \frac{1}{2(n-2)} + \alpha_D - A[\pi\alpha_D]^{\frac{n-2}{n}}. \tag{32}$$

This formula is extremely close to our analytic expressions of ε in the resonance formalism, because both works use a matching procedure of an inner JWKB wavefunction to an exact zero energy outer wavefunction. More precisely, these three formulae are the first terms of an expansion of ε in power of $(\alpha_D)^{1/n}$. For instance, in the case $n = 6$, we know only two nonvanishing terms (in $(\alpha_D)^{2/3}$ and in (α_D)) and these terms are identical in the three formulae, while the higher order terms are surely not meaningful, because of the approximations used in the derivations.

In our previous paper [12], we have introduced a model to evaluate ε. We have defined a cutoff radius r_{c0} such as:

$$\frac{1}{\hbar}\int_{r_{c0}}^{\infty} p(r)\,\mathrm{d}r = \frac{\pi}{2(n-2)} \tag{33}$$

which verifies:

$$r_{c0}\,p(r_{c0}) = \frac{\pi}{4}\hbar \tag{34}$$

a condition which is independent of the n value. We have assumed that equation (34) presents some generality and that it can be used to define a cutoff radius r_c also for non zero energy bound levels by replacing r_{c0} by r_c in this equation. Then, ε is given by:

$$\frac{1}{\hbar}\int_{r_c}^{r_2} p(r)\,\mathrm{d}r = \varepsilon\pi. \tag{35}$$

We have tried to improve the definition of r_c in the case of a non zero energy level. In formula (33), $\frac{\pi}{2(n-2)}$ is the excess of phase for a zero energy bound level. For a vibrational state with a non zero binding energy, this excess of phase is not equal to $\frac{\pi}{2(n-2)}$. This fact induces a bias in formula (34) used for a non zero energy level. To improve the approximation made in this formula, one can remark that the quantity $\frac{\pi}{2(n-2)}$ is also equal to $\pi\left(\alpha_D + \frac{1}{2(n-2)}\right)$ for a zero energy bound state ($\alpha_D = 0$ for this case). As expected, this expression is non constant and varies with the

Table 3. Starting from the experimental values of the binding energy E_b of the highest level (Col. 2), we deduce the quantity α_D. The values α_DWKB1 are obtained without the ε correction (using Eqs. (7, 21)) while this correction is taken into account in the values α_DWKB2 (using formula (37)).The corresponding values of the scattering length are deduced from α_D with formula (39) and they appear in the columns a_WKB1 and a_WKB2. The values of the parameters C_6 and μ appear in Table 2. Our calculations agree well with the published values given in column a_exp, but as α_D is not small in these three cases, the second order JWKB term has not a very large effect.

	E_b (cm^{-1})	α_DWKB1	α_DWKB2	a_WKB1 (a.u.)	a_WKB2 (a.u.)	a_exp (a.u.)
Li	0.416	0.838	0.852	−24.6	−30.8	−27.6 ± 0.5
Na ($F=0$)	0.013	0.431	0.455	52.0	48.6	50.4 ± 2.7
Na ($F=2$)	0.0105	0.393	0.419	57.5	53.7	52 ± 5
						55 ± 1.2
						55 ± 2.7

binding energy of the highest level. Making this replacement in equation (33), the formula defining r_c becomes:

$$r_\mathrm{c}p(r_\mathrm{c}) = 2\pi\left(\alpha_\mathrm{D} + \frac{1}{2(n-2)}\right)\hbar. \tag{36}$$

Thus, with r_c being the solution of this equation for $E(v) \neq 0$ and using equation (35), we obtain an improved integral expression of ε. Unfortunately, it is not easy to write the corresponding analytical formula of ε and we have only made numerical calculations of this new approximation of ε.

We have compared the analytic formulae and the integral model to the numerical results described above in the case $n = 6$ (Fig. 4a) and $n = 3$ (Fig. 4b). In both cases, there is a range of α_D values where neither the second order JWKB formula nor the resonance formula describe precisely the correction term ε. Finally, we can notice that, in the $n = 3$ case, the integral expression of ε is better than the resonant ones.

3.4 Evaluation of the scattering length

Starting from the binding energy of the last bound level, it is possible to deduce an accurate estimate of the scattering length using the analytical formula of the previous section. If the last bound level occurs in an energy range where the JWKB formalism is still valid, using formula (22, 26), we are able to express α_D in terms of the binding energy of this level:

$$\alpha_\mathrm{D} = \frac{[-E(v)]^{\frac{n-2}{2n}}}{H_n} - \frac{1}{2(n-2)} + \frac{n+1}{24\pi(n-2)}\tan\left(\frac{\pi}{n}\right)\frac{H_n}{[-E(v)]^{\frac{n-2}{2n}}}\cdot \tag{37}$$

We assume that the value H_n given by expression (8) is available. If this level occurs in an energy range where the resonance formula is valid, using expressions (22, 28), we can write:

$$\alpha_\mathrm{D} = \frac{1}{\pi}\arctan\left[\frac{\sqrt{-E(v)}}{(AH_n)^{\frac{n}{n-2}}}\right] \tag{38}$$

with A given by (29). Thus, using the definition of α_D (formula (21)) and equation (11), we can express the scattering length a in the following way:

$$a = \bar{a}\left[1 + \frac{\tan\left(\frac{\pi}{n-2}\right)}{\tan(\pi\alpha_\mathrm{D})}\right] \tag{39}$$

with $\bar{a}$ defined by formula (12). This equation is just the Gribakin and Flambaum formula expressed with α_D. Using equation (37) or (38), we can express a directly from the value of the binding energy of the highest level, when one of these two equations is valid *i.e.* when $\alpha_\mathrm{D} \gtrsim 0.4$ (or $E_b \gtrsim 0.1H_n^{\frac{2n}{n-2}}$) for equation (37) and, for equation (38), when $\alpha_\mathrm{D} \lesssim 0.05$ (or $E_\mathrm{b} \lesssim 0.001H_n^{\frac{2n}{n-2}}$) for $n = 6$ or $\alpha_\mathrm{D} \lesssim 0.1$ (or $E_\mathrm{b} \lesssim 0.005H_n^{\frac{2n}{n-2}}$) for $n = 3$.

In the case of the alkali dimers ($n = 6$), recent experiments have given very accurate binding energies of the highest levels in lithium [1] ($a^3\Sigma_u^+$ state of $^7\mathrm{Li}_2$) and sodium [7] ($X^1\Sigma_g^+$ state of Na_2 $F = 0$ and $F = 2$). A very weakly bound level (≈ -0.0053 cm^{-1}) has been seen for the $^{85}\mathrm{Rb}_2$ also [3] but it is not a $l = 0$ level. In the case of lithium and sodium, the energies of the highest levels are $-0.4160(14)$ cm^{-1} for lithium, $-0.0131(7)$ cm^{-1} ($F = 0$) and $-0.0106(7)$ cm^{-1} ($F = 2$) for sodium. All of these binding energies are well within the validity range of the second order JWKB approximation. In Table 3, we present the values of α_D and of the scattering length obtained in these three cases. The results labeled WKB1 are obtained by neglecting the ε correction (using Eqs. (7, 21) to deduce α_D) while those labeled WBKB2 include this correction (using formula (37) to deduce α_D). Then, the scattering length is deduced from α_D with formula (39). In the lithium case, our result is $a \approx -30.8a_0$ while the best published value is $-27.6\pm0.5a_0$ [37]. For the sodium $F = 2$ case, many recent results give the same value: $a = 52\pm5a_0$ using p-wave resonance analyses [2], $a = 55.4\pm1.2a_0$ using Feschbach resonance data [8] and $a = 55.3 \pm 2.7a_0$ from the nodal structure of the ground state wavefunction [7]. Our direct method gives the result $a \approx 53.5a_0$. Finally for the sodium $F = 0$ case, the result of Crubellier *et al.* is $a = 50.4 \pm 2.7a_0$ while our result is $a \approx 48.4a_0$. In all the

Table 4. Comparison between different calculations of scattering length: theoretical results obtained with (a_{WKB2}) or without (a_{WKB1}) the second order JWKB quantization condition correction, using the resonance formalism (a_{r2}) and numerical calculation (a_{num}). The present calculations are done in the cesium (see Tab. 2) and with a variable well depth D_{e} given in the first column. The binding energy of the highest level E_{b} is given in the second column.

D_{e} (cm^{-1})	E_{b} (cm^{-1})	a_{WKB1} (a.u.)	a_{WKB2} (a.u.)	a_{r2} (a.u.)	a_{num} (a.u.)
3631	0.999×10^{-6}	−470.97	/	1046.43	1082.72
3638	0.139×10^{-4}	707.48	/	349.84	373.69
3644	0.406×10^{-4}	326.48	246.52	244.01	257.97
3665	0.305×10^{-3}	138.55	129	/	129.6
3695	0.0014	32.9	25.6	/	25.8
3710	0.0024	−80.5	−100.4	/	−99.95
3715	0.0028	−181.4	−223.6	/	−222.8
3720	0.0033	−471.52	−650.37	/	−646.77

Table 5. For the same cases presented in Table 4, we compare various approximate values of α_{D} to our numerical estimate of this quantity.

D_{e} (cm^{-1})	α_{DWKB1}	α_{DWKB2}	α_{Dr2}	α_{Dnum}
3631	−0.0528	/	0.0315	0.0304
3638	0.0487	/	0.1130	0.1040
3644	0.1233	0.1773	0.1796	0.1671
3665	0.3615	0.3890	/	0.3871
3695	0.6840	0.7010	/	0.7001
3710	0.8424	0.8562	/	0.8559
3715	0.8949	0.9080	/	0.9078
3720	0.9473	0.9598	/	0.9596

cases, the value obtained by our method is in quite good agreement with the published values. However, as shown in Table 3, the WKB1 results and the WKB2 results have comparable accuracy in these three cases, because the ε term remains small.

To show more clearly the interest of using the quantization condition correction, Table 4 presents the values of scattering length obtained for a model LJ(12-6) potential in a case representative of the cesium dimer (parameters listed in Tab. 2). The a_{num} values are obtained by our numerical calculation already used in Section 2.4 and they serve to test our approximate results. We have also calculated a with our formulas (37–39) and with the normal first order JWKB formula. These calculations have been made for 8 different potentials with scattering length varying from $1100a_0$ to $-650a_0$ covering thus the complete range of α_{D} values which are collected in Table 5. We obtain a very good estimate of the scattering length a in all cases, by using either equation (37) (when α_{D} is large) or equation (38) (when α_{D} is small). Our estimate remains good even when α_{D} is between 0.05 and 0.4 where none of our formulae represents accurately ε. On the contrary, the first order JWKB formula gives poor estimates except for intermediate values of α_{D} where the scattering length is a slowly varying function of α_{D}.

Finally, it is important to remark that the present calculations depend only on the knowledge of the long range C_6 coefficient and do not require any knowledge of the inner part of the potential. The value of the scattering length has been shown to be highly sensitive [7] to the C_6 value and the uncertainty on this quantity is not negligible. The precise determination of the binding energy of the highest level is also very difficult and a small modification of this value can strongly shift the α_{D} value and thus the scattering length.

4 Conclusion

We have presented a refined analysis of the correction to the quantization condition for the highest vibrational levels in a molecular potential. This effect has two main characteristics. First, this is a quantum threshold effect similar to the one which occurs in the low energy part of the continuum. Second, this is a general, quite universal effect, which does not depend of the value of the long range C_n coefficient but which depends strongly on the power n of the leading term of the potential at long range.

In this paper, we have introduced the question by recalling the Near Dissociation Expansion of LeRoy, Bernstein and Stwalley and the Gribakin and Flambaum formula giving the scattering length. We have tested the Gribakin and Flambaum formula in the case of Lennard-Jones 12-6 potentials thus showing its very good accuracy. We have compared our numerical estimates of the number of bound states in Lennard-Jones 12-6 potentials to the previous knowledge, thus showing the need to improve previous formulae by a second order JWKB term.

We have then discussed the phase correction term ε introduced by us to correct the first order JWKB formula near the dissociation limit. The quantity ε has been estimated numerically for potentials behaving like r^{-6} or r^{-3} at long range and these numerical results have been compared to several analytical approximations. One approximation is based on the second order JWKB term, following the ideas of LeRoy and coworkers, and is valid when the highest level is not too close to the dissociation limit. The other approximations, which are valid in the opposite case, rely on the exact zero energy wavefunction.

Finally, we have shown that, in the case $n = 6$, the knowledge of an analytical approximation of ε can be used to evaluate the scattering length when one knows the energy of the highest vibrational level and the long range C_6 coefficient.

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