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Rotational structures of long-range diatomic molecules

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Abstract. We present a systematic understanding of the rotational structure of a long-range (vibrationally highly-excited) diatomic molecule. For example, we show that depending on a quantum defect, the least-bound vibrational state of a diatomic molecule with $-C_n/r^n$ $(n > 2)$ asymptotic interaction can have only 1, 2, and up to a maximum of $n-2$ rotational levels. A classification scheme of diatomic molecules is proposed, in which each class has a distinctive rotational structure and corresponds to different atom-atom scattering properties above the dissociation limit.

PACS. 33.15.Mt Rotation, vibration, and vibration-rotation constants – 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.) – 03.75.Nt Other Bose-Einstein condensation phenomena – 03.75.Ss Degenerate Fermi gases

1 Introduction

How fast can we rotate a molecule before breaking it [1,2]? How does a rotational series terminates at the dissociation limit? How many rotational levels are there for a diatomic molecule in its last (least-bound), or next-to-last, vibrational state? These intriguing, and closely related, questions are taking on a new dimension of practical importance as our ability to make large samples of long-range molecules (vibrational highly-excited molecules) [3–13], and even condensates of long-range molecules [14–16], continues to grow. To understand the properties of a long-range molecule, especially how it responds to external perturbations such as collision with other atoms, we need not only the properties of a particular molecular state, such as the least-bound s state. We also need to know what are the states around it. It is this global structure of states that is the focus of this work.

One approach to this problem is to compute the universal spectra for each type of long-range interaction, $-C_n/r^n$, as we have done previously for $n = 6$ [17,18] and $n = 3$ [19], and simply observe them. This would, however, be very tedious and can never be completely inclusive. Our approach here is based on the recognition that the global structure of states, not including specific values for binding energies, depends only on the zero-energy wave function, more specifically, on its number of nodes as a function of both the angular momentum quantum number l and the exponent n characterizing the long-range interaction.

Our results, and answers to the questions raised above, can be summarized in two simple formulas that will be derived later in the article. The first gives the dependence of the number of bound levels on the angular momentum l for a quantum system with $-C_n/r^n$ $(n > 2)$ long-range interaction

$$N_l = \mathrm{Int}\left[N_0 + \mu^c - \frac{1}{n-2}l\right]. \tag{1}$$

Here $\mathrm{Int}[x]$ represents the greatest integer less than or equal to x. N_l is the number of bound levels of angular momentum l. N_0 is the number of s wave bound levels. μ^c is a quantum defect, to be defined later, that has a range of $0 \leq \mu^c < 1$.

The second formula relates the quantum defect to the s wave scattering length

$$a_{0s} = \bar{a}_{0s}\frac{\tan(\pi\mu^c) + \tan(\pi b)}{\tan(\pi\mu^c)}. \tag{2}$$

Here $a_{0s} = a_0/\beta_n$ is the s wave scattering length, a_0, scaled by the length scale $\beta_n = (2\mu C_n/\hbar^2)^{1/(n-2)}$ associated with the long-range interaction; $b = 1/(n-2)$; and

$$\bar{a}_{0s} = \cos(\pi b)\left[b^{2b}\frac{\Gamma(1-b)}{\Gamma(1+b)}\right], \tag{3}$$

is the mean s wave scattering length of Gribakin and Flambaum [20], scaled by β_n.

The consequences of these results are easily understood and are discussed in Section 3. Equation (1) is derived in Section 2. It is another example of universal properties at length scale β_n, as discussed in a more general terms

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in two recent publications [21,22]. This universal property is followed by all molecules in varying degrees. Deviations from it and other issues are discussed in Section 4. A primer of the angular-momentum-insensitive quantum-defect theory (AQDT) [17,18], which is the foundation of this work, can be found in Appendix A.

2 Derivation of equation (1)

Equation (1) may be derived using two different methods. One is to apply AQDT [17,18], the version for arbitrary $n > 2$ as outline in [21] and Appendix A, to the zero-energy diatomic state. This approach is discussed briefly in Appendix A. The other approach is the method of effective potential [21,22]. It is this latter method that we present here, for the purpose of further promoting this powerful concept. While it makes no difference in this particular case, for more complex systems, such as quantum few-body or quantum many-body systems [22] where no analytic solutions are available, the method of effective potential may be the only way to uncover universal properties at different length scales. The results would, of course, be mostly numerical in those cases. But a numerical solution done right can indeed yield universal behavior [22].

The method of effective potential is very simple. It states that for a physical observable that depends only on states around the threshold, such as the number of nodes of the zero-energy wave function that we are looking at here, its universal behavior at length scale β_n can be derived from any potential that has the right asymptotic behavior and is strongly repulsive at short distances. Specifically, a universal result at length scale β_n is obtained from the corresponding result for an effective potential by taking a proper limit that eliminates the shorter length scales while keeping the short-range K matrix, $K^c(0,l)$ ([17] and Appendix A), to be a constant for one particular l [21,22].

We take here, for simplicity, a hard-sphere with an attractive tail (HST),

$$V_{\mathrm{HST}}(r) = \begin{cases} \infty & , r \le r_0 \\ -C_n/r^n & , r > r_0 \end{cases}, \tag{4}$$

as our effective potential. Its number of bound levels for angular momentum l is given by ([21] and Appendix A)

$$N_{\mathrm{HST}}(l) = \begin{cases} m & , j_{\nu_0,m} \le y_0 < j_{\nu_0,m+1} \\ 0 & , y_0 < j_{\nu_0,1} \end{cases}, \tag{5}$$

where $y_0 = [2/(n-2)](\beta_n/r_0)^{(n-2)/2}$, $\nu_0 = (2l+1)/(n-2)$, and $j_{\nu_0,m}$ ($m \ge 1$) is the mth zero of the Bessel function $J_{\nu_0}(x)$ [23].

Its K^c parameter at zero energy is given by ([21] and Appendix A).

$$K^c_{\mathrm{HST}}(0,l) = -\frac{J_{\nu_0}(y_0)\cos(\pi\nu_0/2) - Y_{\nu_0}(y_0)\sin(\pi\nu_0/2)}{J_{\nu_0}(y_0)\sin(\pi\nu_0/2) + Y_{\nu_0}(y_0)\cos(\pi\nu_0/2)}, \tag{6}$$

where J and Y are the Bessel functions [23].

In the limit of $r_0 \to 0+$ that eliminates the shorter length scale (see [22] for a more precise definition), $y_0 \gg 1$, and the roots of the Bessel function are given by [24]

$$j_{\nu_0,m} \to (m + \nu_0/2 - 1/4)\pi. \tag{7}$$

$K^c_{\mathrm{HST}}(0,l)$ becomes an l-independent constant

$$K^c_{\mathrm{HST}}(0,l) \to K^c = \tan(y_0 + \pi/4). \tag{8}$$

Defining the quantum defect, $\mu^c(\epsilon,l)$, to be a parameter in a range of $0 \le \mu^c < 1$ and related to K^c by

$$K^c(\epsilon,l) = \tan\left[\pi\mu^c(\epsilon,l) + \frac{\pi}{2(n-2)}\right], \tag{9}$$

it is clear that $\mu^c_{\mathrm{HST}}(0,l)$ also becomes an l-independent constant

$$\mu^c_{\mathrm{HST}}(0,l) \to \mu^c = \frac{y_0}{\pi} + \frac{1}{4} - \frac{1}{2(n-2)} - j, \tag{10}$$

where j is an integer chosen such that μ^c falls in the range of $0 \le \mu^c < 1$.

Combining these results, the number of bound levels of angular momentum l for a HST potential can be written in the limit of $r_0 \to 0+$ as

$$N_{\mathrm{HST}}(l) \to m, \quad m \le j + \mu^c - \tfrac{1}{n-2}l < m+1, \tag{11}$$

or,

$$N_{\mathrm{HST}}(l) \overset{r_0 \to 0+}{\longrightarrow} \mathrm{Int}\left[j + \mu^c - \frac{1}{n-2}l\right]. \tag{12}$$

Note that the result on the right-hand-side of this equation is now no longer just a property of the HST potential, but a universal property at length scale β_n, applicable to any quantum system with the same long-range behavior and has a β_n that is much longer than other length scales in the system [21,22].

Since $0 \le \mu^c < 1$, the integer j in equation (12) is simply the number of bound levels for $l = 0$. Equation (1) is thus derived. It is easy to show that starting from a Lennard-Jones $LJ(n, 2n-2)$ effective potential [21] (see also Sect. 4.2) leads to identical result. And again, the same result can also be derived by applying AQDT to the zero-energy diatomic state, as outlined in Appendix A.

This derivation illustrates one of the key differences between the method of effective potential [21,22] and the pseudopotential method [25]. In the latter method, a different pseudopotential is required for each partial wave. And each pseudopotential has at least one independent parameter to characterize the scattering of that particular partial wave. Without another theory relating scattering of different partial waves, no universal l-dependence of any kind can be established. (This is in addition to its well known limitations in describing bound states.) In contrast, a single effective potential is used to describe all l. This is possible because a single parameter in AQDT describes a multitude of angular momentum states (see [17,18] and Appendix A). Put it in another way. Scattering of different partial waves are related, and so are the bound spectra

Table 1. Classification of diatomic molecules with $-C_n/r^n$ $(n > 2)$ long range interaction using quantum defect. Here $L_{max,v}$ is the maximum rotational quantum number for the vibrational state v. $\Delta v = v_{max} - v$. $a_{0s} = a_0/\beta_n$ is the scaled s wave scattering length. Note that some of the rotational states may be excluded for identical particles. Also note that scattering length has no definition for $n = 3$.

Class j	Range of μ^c	$L_{max,v}(j)$	Range of a_{0s}
0	$0 \le \mu^c < b$	$0 + (n-2)\Delta v$	$2\bar{a}_{0s} < a_{0s} \le \infty$
1	$b \le \mu^c < 2b$	$1 + (n-2)\Delta v$	$\vdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$
$n-3$	$(n-3)b \le \mu^c < 1$	$n - 3 + (n-2)\Delta v$	$-\infty < a_{0s} \le 0$

of different partial waves. These relations are determined by the long-range interaction ([17,18] and Appendix A), and are incorporated automatically in an effective potential [21]. The universal property described by equation (1) is but one reflection of the resulting systematics.

3 Classification of molecules using quantum defect

Let us first state that we do not include explicitly the effect of statistics when atoms are identical. It would make our statements unnecessarily complex without introducing any new physics. In specific applications, all one needs to do is to exclude states that cannot satisfy the symmetry requirement (see, for example, [26]), as needed.

The physical implications of equation (1) can be easily understood by noting that $N_0 - 1$ is *the* maximum vibrational quantum number, v_{max}, while $N_l - 1$ is the maximum vibrational quantum number, $v_{max,l}$, that can support a rotational state of angular momentum l. A vibrational state v can have all l for which $v_{max,l} \ge v$. Let $L_{max,v}$ to be the maximum rotational quantum number for vibrational state v. From equation (1), it is the maximum l that can satisfy

$$v = \mathrm{Int}\left[v_{max} + \mu^c - \frac{1}{n-2}l\right], \tag{13}$$

which gives

$$L_{max,v} = (n-2)(v_{max} - v) + \mathrm{Int}\left[(n-2)\mu^c\right]. \tag{14}$$

This result suggests the classification of molecules into $n - 2$ classes, each corresponding to an equal interval of $b = 1/(n-2)$ in the quantum-defect space. For Class j with $jb \le \mu^c < (j+1)b$, where $0 \le j \le n-3$, we have $j \le (n-2)\mu^c < j+1$, and therefore

$$L_{max,v}(j) = j + (n-2)(v_{max} - v). \tag{15}$$

Thus each class of molecules corresponds to a unique rotational structure that terminates at $L_{max,v}(j)$. This classification is summarized in Table 1. In particular, it means that the least-bound vibrational state can have 1 (Class 0), 2 (Class 1), and up to a maximum of $n - 2$ (Class $n - 3$) rotational levels, depending on the quantum defect of the molecule. For the next-to-last vibrational state, add $n - 2$ rotational levels to each class, and so on for lower vibrational states.

What makes this classification useful is that each class not only has a distinctive rotational structure, it also corresponds to distinctive atom-atom scattering properties above the dissociation limit. In particular, each class of molecules corresponds to a distinctive (non-overlapping) range of scattering length, which can be determined from equation (2) and is summarized in Table 1.

Equation (2) is derived from the definition of the mean scattering length [20], equation (3), the definition of the quantum defect, equation (9), and the following rigorous relation between K^c and the s wave scattering length ([21] and Appendix A)

$$a_{0s} = \left[b^{2b}\frac{\Gamma(1-b)}{\Gamma(1+b)}\right]\frac{K^c(0,0) + \tan(\pi b/2)}{K^c(0,0) - \tan(\pi b/2)}, \tag{16}$$

which is similar to the relation between scattering length and a semiclassical phase as derived by Gribakin and Flambaum [20]. These equations combine to give

$$a_{0s} = \bar{a}_{0s}\frac{\tan[\pi\mu^c(0,0)] + \tan(\pi b)}{\tan[\pi\mu^c(0,0)]}, \tag{17}$$

which is the exact relation between the scattering length and the quantum defect. It is the more rigorous representation of equation (2), applicable even when the system deviates from the universal behavior (see Sect. 4.3 and Appendix A).

With the correspondence between quantum defect and scattering length, our classification of molecules can translate into other general statements, such as, (a) the least-bound vibrational state of a diatomic molecule with $a_{0s} \ge 2\bar{a}_{0s}$ has only a single rotational state. (b) The least-bound vibrational state of a diatomic molecule with negative scattering length has $n - 2$ rotational states. It is worth noting that molecules with negative scattering length all fall into a single class, Class $n - 3$, while molecules with positive scattering length separate into $n - 3$ classes, from Class 0 to Class $n - 4$. A similar feature was first noted by Gribakin and Flambaum [20].

The different scattering properties for different classes are not restricted to the s wave. In fact, more interesting differences occur for higher partial waves. For example, Class 0 does not have a p wave bound state for the last vibrational level. This p state, which would have been bound for $\mu^c \geq b$, does not disappear completely. It shows itself as p wave shape-resonance above the threshold, which becomes infinitely narrow (infinitely long-lived) as one approaches $\mu^c = b$ from the side of Class 0. In general, a Class j system, $0 \leq j \leq n-3$, is the one that has a shape-resonance of $l = j+1$ closest to the threshold. The detailed properties of these resonances are however beyond the scope of this article (see, e.g. [17,27–29]).

The critical values of $\mu^c = jb$, $0 \leq j \leq n-3$, that are the boundaries between different classes correspond to having bound or quasibound states of angular momenta $l = j + (n-2)m$ (m being a non-negative integer) right at the threshold (Appendix A). They have vibrational quantum numbers of $v = v_{max} - m$, respectively. This is a generalization of some of the results in [18] to the case of arbitrary $n > 3$. Note that the wave functions for zero-energy bound or quasibound states are well defined and are given in the region of long-range potential by (Appendix A)

$$u_{\epsilon=0l}(r) = A r_s^{1/2} J_{\nu_0}(y), \tag{18}$$

where $r_s = r/\beta_n$ is a scaled radius, and $y = [2/(n-2)] r_s^{-(n-2)/2}$. This wave function has an asymptotic behavior of $1/r^l$ at large r, thus representing a true, normalizable, bound state for $l > 0$, and a quasibound (not normalizable) state for $l = 0$. The fact that the s-wave wave function in the effective-range theory becomes completely meaningless when $a_0 = \infty$ is only a limitation of that particular theory, not a reflection of any physical reality.

4 Discussions

We discuss here some special cases, deviations from the universal behavior, and how they might be treated.

4.1 The case of n = 3

Our results, equations (1) and (15), are applicable to $n = 3$, even though the scattering length has no definition in this case (for any l) [30,31]. Specifically, equation (15) predicts that quantum systems with $n = 3$ have only a single class (Class 0) with $L_{max,v} = v_{max} - v$. In other words, the last vibrational state for $n = 3$ has only a single rotational state, an s state. The next-to-last vibrational state has two rotational levels, and so forth. This prediction is confirmed by the analytic solution for $-C_3/r^3$ potential [19,31].

4.2 The special case of LJ(n, 2n − 2) potentials

For a set of Lennard-Jones potentials $LJ(n, 2n-2)$ ($n > 2$) defined by

$$V_{LJn}(r) = -C_n/r^n + C_{2n-2}/r^{2n-2}, \tag{19}$$

the number of bound levels for any l is given by ([21] and Appendix B)

$$N_{LJn}(l) = \begin{cases} \mathrm{Int}\left[z_0 + \frac{1}{2} - \frac{\nu_0}{2}\right] & , z_0 \geq (\nu_0+1)/2 \\ 0 & , z_0 < (\nu_0+1)/2 \end{cases}, \tag{20}$$

where $\nu_0 = (2l+1)/(n-2)$ and $z_0 = (\beta_n/\beta_{2n-2})^{n-2}/[2(n-2)]$, in which β_{2n-2} is the length scale associated with the C_{2n-2}/r^{2n-2} interaction. Thus for a $LJ(n, 2n-2)$ potential, the universal dependence of the number of bound levels on l, as specified by equation (1), is exact, true even when β_{2n-2} is comparable to β_n and the corresponding potential is so shallow as to support only a single or a few bound states.

This result implies that to break the universal dependence on l, one needs not only a short-range interaction, but the behavior of this interaction also has to be different from $LJ(n, 2n-2)$.

4.3 Deviations from the universal behavior

The key to understand qualitatively the deviation from the universal behavior is to recognize the origin of this universality. The universal l-dependence originates from the l-independence of $K^c(0,l)$ ([17] and Appendix A), which is a result of both the small mass ratio m_e/μ, where m_e is the electron mass and μ is the reduced mass of the molecule (not to be confused with the quantum defect μ^c), and the condition of $\beta_n \gg r_0$ where r_0 is a representative of other length scales in the system. It is typically the range of exchange interaction with a magnitude around 20−60 a.u.

With this understanding, it is clear that the universal behavior of equation (1) should be followed by all molecules to some degree. The mass ratio m_e/μ is always small and can be taken for granted. (This is why we don't always mention it.) And almost by definition, β_n *is* the longest length scale in the problem, otherwise it would not, and should not have been called the long-range interaction.

It is also clear that the universal behavior is best followed by the states with highest vibrational quantum numbers. For example, consider our prediction of $L_{max,v}(j) = j + (n-2)(v_{max} - v)$. For the least-bound vibrational state with $v = v_{max}$, it would only require l-independence of K^c over a range of $\Delta l = n-2$. In comparison, the same result applied to $v = v_{max} - 9$ would require l-independence of K^c over 10 times that range, which generally becomes considerably worse (depending also on n, and other details of the short-range interaction).

As far as predictions for the last few vibrational states (long-range molecules) are concerned, there is no need to worry about deviation except when μ^c is very close to one of the critical values of $\mu^c = jb$, where a small l-dependence may mean the difference between a bound state and a shape resonance.

When necessary, deviations from the universal behavior can be treated within the AQDT framework. All we need is to count the nodes of the zero-energy wave functions more carefully. As discussed in Appendix A, AQDT is an exact formulation and an excellent platform for exact numerical calculations. This also applies to node-counting: integrate the Schrödinger equation at zero energy and count the nodes up to a distance where $K^c(0,l)$ has converged to a desired accuracy [one computes $K^c(0,l)$ by matching the integrated wave function to that given by Eq. (A.8) at different radii r. As a function of this matching radius, $K^c(0,l)$ converges to a r-independent constant when the potential becomes $-C_n/r^n$ and the wave function becomes that of Eq. (A.8)]. Adding to that the number of nodes beyond this distance, which can now be calculated analytically, gives one the total number of nodes.

One could also try to find if there are any systematics in the deviation by going to the next, shorter, length scale. Any such attempt would however be necessarily system-specific and will be deferred to specific applications. Examples of the universal rotational structure for $n = 6$ can already be found in [17,18], though they were not discussed explicitly. It was the simple structures observed there that motivated this work.

5 Conclusion

In conclusion, we have shown that the rotational structure of a long-range molecule follows a simple universal behavior that is characterized by two parameters, the exponent n of the long-range interaction $-C_n/r^n$, and a quantum defect, which is related in a simple way to the s wave scattering length whenever the latter is well defined ($n > 3$). The resulting classification scheme gives a simple qualitative description of both the rotational structure of a long-range molecule and the corresponding atom-atom scattering properties above the dissociation threshold.

Finally, getting back to one of the questions at the beginning that we have not answered explicitly: how fast can we rotate a molecule before breaking it? The answer is, of course, $L_{max,v}$ units of angular momenta, which is generally a very small number for long-range molecules.

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Appendix A: AQDT: a primer

We give here a brief review of the angular-momentum-insensitive quantum defect theory (AQDT) [17,18]. The focus will be on the conceptual aspects, and issues directly related to this particular work. We point out that there are a number of different quantum-defect formulations for diatomic systems [26,32–35]. There are also quantum-defect analysis [36,37], and numerical methods that incorporate the concepts of quantum-defect theory [38]. Only our formulation is briefly reviewed here.

Consider a radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) - \epsilon\right] u_{\epsilon l}(r) = 0, \quad \text{(A.1)}$$

where $V(r)$ becomes $-C_n/r^n$ beyond a distance r_0, which corresponds typically to the range of exchange interaction with a magnitude around 20−60 a.u.

In AQDT, the wave function in the region of long-range interaction ($r \geq r_0$) is written as a linear superposition of a pair of reference functions

$$u_{\epsilon l}(r) = A_{\epsilon l}[f^c_{\epsilon_s l}(r_s) - K^c(\epsilon,l) g^c_{\epsilon_s l}(r_s)], \quad \text{(A.2)}$$

which also serves to define the short-range K matrix $K^c(\epsilon,l)$. The functions f^c and g^c are solutions for the long-range potential $-C_n/r^n$ [31,39]. Their notations reflect the fact that with proper scaling and normalization, f^c and g^c depend on r only through a scaled radius $r_s = r/\beta_n$ and on energy only through a scaled energy [31,39]

$$\epsilon_s = \frac{\epsilon}{(\hbar^2/2\mu)(1/\beta_n)^2}. \quad \text{(A.3)}$$

Note that for the purpose of cleaner notion for arbitrary n, we have abandoned the factor of 16 used previously for $n = 6$ [17,18,28,39], and the factor of 4 used previously for $n = 3$ [19,31].

Much of the art of a quantum defect theory [40–43] is in choosing f^c and g^c that best reflect the underlying physics. For a molecule, the wave function at short distances is nearly independent of l because the rotational energy is small compared to electronic energy (originated from the small mass ratio m_e/μ). AQDT takes advantage of this fact by picking a pair of solutions for $-C_n/r^n$ potential that have not only energy-independent, but also l-independent behavior at short distances (possible because $n > 2$) [17,21,22]:

$$f^c_{\epsilon_s l}(r_s) \xrightarrow{r \ll \beta_n} (2/\pi)^{1/2} r_s^{n/4} \cos(y - \pi/4), \quad \text{(A.4)}$$

$$g^c_{\epsilon_s l}(r_s) \xrightarrow{r \ll \beta_n} -(2/\pi)^{1/2} r_s^{n/4} \sin(y - \pi/4), \quad \text{(A.5)}$$

where $y = [2/(n-2)] r_s^{-(n-2)/2}$.

With this choice of reference pairs, matching to wave function at short distances yields an K^c that is nearly independent of l, provided that r_0 is much smaller than β_n so that the reference functions at r_0 are well represented by their l-independent form of equations (A.4–A.5).

An approximately l-independent K^c thus reflects the underlying physics that while the angular momentum dependence is very important for long-range molecules and atom-atom scattering at low energies, it is important only at large distances where its effects can be incorporated analytically. This is the physical origin of why a single parameter in AQDT is often capable of describing a multitude of angular momentum states [17,18,21].

The approximate energy-independence of K^c, under the same condition of $\beta_n \gg r_0$ is fairly standard [40,42]. It is both because the reference functions have been chosen to be energy-independent at short distances, and because the short-range wave function varies with energy on a scale of $(\hbar^2/2\mu)(1/r_0)^2$, much greater than the corresponding energy scale associated with the long-range interaction, which is $(\hbar^2/2\mu)(1/\beta_n)^2$ [19].

In a multichannel theory that takes into account the hyperfine structures of atoms (starting from the formulation in [26]), the concepts of AQDT, and the concept of l-independence in particular, remain unchanged and lead to an even greater reduction in the number of parameters required for a complete characterization of the system [44,45].

We emphasize that AQDT is an exact formulation that does not require either the energy-independence or the l-independence of K^c. It is simply a good framework, especially conceptually, to take advantage of them when they are there ($\beta_n \gg r_0$). The parameterizations that we often use to extract universal behaviors should not distract from the fact that AQDT also provides an excellent platform for exact numerical calculations, whether single channel [21] or multichannel. This is especially true close to the dissociation limit, where matching to analytic solutions for $-C_n/r^n$ potential to obtain $K^c(\epsilon, l)$ converges much faster than matching to free-particle solutions to obtain the standard K matrix. The calculations in [21] are all based on this platform.

A major task of AQDT is, of course, finding the reference functions. This is in general highly nontrivial [31,39], especially analytically. No solution is yet available for $n = 5$ at $\epsilon \neq 0$. This difficulty is however not a problem here as we need only the zero-energy reference functions, which can be easily found for arbitrary n and l [17,46]

$$f^c_{\epsilon_s=0l}(r_s) = [2/(n-2)]^{1/2} r_s^{1/2}[J_{\nu_0}(y)\cos(\pi\nu_0/2) - Y_{\nu_0}(y)\sin(\pi\nu_0/2)], \tag{A.6}$$

$$g^c_{\epsilon_s=0l}(r_s) = -[2(n-2)]^{1/2} r_s^{1/2}[J_{\nu_0}(y)\sin(\pi\nu_0/2) + Y_{\nu_0}(y)\cos(\pi\nu_0/2)], \tag{A.7}$$

where $\nu_0 = (2l+1)/(n-2)$. With these reference functions, the zero-energy wave function can be written either as

$$u_{\epsilon=0l}(r) = A_l[f^c_{\epsilon_s=0l}(r_s) - K^c(0,l)g^c_{\epsilon_s=0l}(r_s)], \tag{A.8}$$

or as

$$u_{\epsilon=0l}(r) = A'_l r_s^{1/2}[J_{\nu_0}(y)\cos(\alpha_l) + Y_{\nu_0}(y)\sin(\alpha_l)], \tag{A.9}$$

where $\alpha_l = \pi[\mu^c(0,l) - lb]$ with the quantum defect $\mu^c(\epsilon, l)$ being defined in terms of $K^c(\epsilon, l)$ by equation (9).

The parameters K^c and μ^c both represent the same physics. K^c is more convenient in computation, while μ^c is able to represent all quantum systems in a finite parameter space of $[0, 1)$. In comparison, K^c can take any value from $-\infty$ to $+\infty$.

Equation (5) is a result of node-counting the wave function, given exactly by equation (A.9), from r_0 to infinity ($y = 0$ to y_0) [24]. Equation (6) is obtained by imposing the boundary condition $u_{\epsilon=0l}(r = r_0) = 0$. Equation (16) is obtained by comparing the asymptotic behavior of $u_{\epsilon=0l}(r)$ (for $l = 0$) at large r with the corresponding expansion that defines the s wave scattering length.

$$u_{\epsilon=0l=0}(r) \to A(r - a_0). \tag{A.10}$$

The derivation of equation (1) in AQDT is straightforward. In the limit of $r_0 \ll \beta_n$, the number of nodes of the zero-energy wave function inside r_0 is an l-independent constant [to a degree measured by the l-independence of $K^c(0,l)$]. Counting the number of nodes of the outside wave function, equation (A.9), from r_0 to infinity ($y = 0$ to y_0) [24], and ignoring the l-dependence of $\mu^c(0,l)$ leads to equation (1). From this derivation, it is clear that deviation from the universal behavior is measured by the degree to which $\mu^c(0,l)$ or $K^c(0,l)$ is independent of l.

Having a bound or quasibound state right at the threshold corresponds to the boundary condition of $u_{\epsilon=0l}(r) \to 0$ (or a finite constant for $l = 0$) in the limit of $r \to \infty$. Define

$$x_l(\epsilon) \equiv \tan[\pi\mu^c(\epsilon,l) - \pi lb]. \tag{A.11}$$

From equation (A.9), the condition for a bound state at the threshold is clearly

$$x_l(0) = \tan[\pi\mu^c(0,l) - \pi lb] = 0, \tag{A.12}$$

which translates into $\mu^c(0,l) = jb$, $0 \leq j \leq n-3$, for having bound or quasibound states of angular momenta $l = j + (n-2)m$ (m being a non-negative integer) right at threshold, with corresponding wave functions given by equation (18). In terms of K^c, the same condition takes the form of

$$K^c(0,l) = \tan\left[\frac{1}{n-2}\left(l + \frac{1}{2}\right)\pi\right], \tag{A.13}$$

which is a generalization of the condition in [18] to the case of arbitrary n. Note that the conditions expressed in the form of equations (A.12, A.13) are exact, with no assumption on the l-independence of either parameter. The universal behavior corresponds to when the l-dependence can be ignored ($\beta_n \gg r_0$).

The $x_l(\epsilon)$ parameter defined by equation (A.11) has also other applications. For example, for $\mu^c(0,l) \gtrsim jb$, $x_l(0) \gtrsim 0$ is a convenient expansion parameter for describing bound states of angular momenta $l = j + (n-2)m$ (m being a non-negative integer) that are close to the threshold. $x_l(\epsilon)$ is also closely related to the $K^0_l(\epsilon)$ matrix used in reference [28], simply by $K^0_l(\epsilon) = -x_l(\epsilon)$. With this relation, all the results of reference [28] can be rewritten in terms of either K^c or μ^c. Making use of the l-independence of either parameter in these results can lead, for example, to a relation between the p wave and the s wave scattering lengths.

Reference [28] offers a lesson on the importance of picking reference functions. The f^0 and g^0 functions in references [28,39], which define K^0, differ from f^c and g^c only by a linear transformation. But because the resulting $K^0_l(\epsilon) = -\tan[\pi\mu^c(\epsilon,l) - \pi lb]$ did depend on l, relationships among scattering and bound spectra of different partial waves were not recognized until much later [17,18]. Reference [28] was only able to take advantage of the energy-independence of K^0_l to show, for example, that the effective range and the scattering length are not independent, but are related in a way determined by the long-range interaction. The same conclusion was also reached independently by Flambaum et al. using a different approach [47].

Appendix B: Derivation of the results for LJ(n, 2n − 2) potentials

The analytic results for $N_{LJn}(l)$, equation (20), and $K^c_{LJn}(0,l)$ given in reference [21] [and therefore $\mu^c_{LJn}(0,l)$, and of course a_{0s}] are derived from the *zero*-energy solution of the radial Schrödinger equation, equation (A.1), for the class of potentials defined by equation (19). Instead of giving all the tedious mathematical details, we will simply note its relationship to the harmonic oscillator solution, as they have the same underlying mathematical structure.

Upon a transformation $x = (r/\beta_n)^\alpha$ and $u_l(r) = x^{-(\alpha-1)/(2\alpha)}v_l(x)$ with $\alpha = -(n-2)/2$, the corresponding equation at *zero* energy becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{\hbar^2\gamma(\gamma+1)}{2\mu x^2} + \frac{1}{2}\mu\omega^2 x^2 - E_e\right] v_l(x) = 0, \tag{B.1}$$

with $\gamma + 1/2 = [2/(n-2)](l+1/2)$. Thus for the class of potentials given by equation (19), the solution of the radial Schrödinger equation at *zero* energy is equivalent to the solution of a 3-D isotropic harmonic oscillator with an effective angular momentum γ, a effective frequency determined by $\hbar\omega = (\hbar^2/2\mu)(2/|\alpha|)(\beta_{2n-2}/\beta_n)^{n-2}(1/\beta_n)^2$, *at an effective energy (not zero)* $E_e = (\hbar^2/2\mu)(1/\alpha^2)(1/\beta_n)^2$. From this correspondence, both results are easily deduced. For example, the number of bound levels is simply the number of harmonic oscillator levels below, and including E_e.

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