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Angular-momentum-insensitive quantum-defect theory for diatomic systems

Bo Gao
Department of Physics and Astronomy, University of Toledo, Toledo, Ohio 43606
and Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
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We show that the highly excited rovibrational spectra of a diatomic molecule and the closely related slow atomic collision processes contain more systematics and require less parameters to characterize than the Rydberg spectrum of an atom. In the case of a single channel, e.g., we show that a *single* short-range parameter gives a complete description of slow collisions for practically all angular momenta, and covers an energy range of hundreds of millikelvins. The *same* parameter also describes the highly excited rovibrational spectra in the threshold region, including states of different angular momenta. Sample applications and predictions of the theory are presented, including comparisons with experiment.

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With recent developments such as the analytic solutions of the Schrödinger equation for $1/r^6$ and $1/r^3$ potentials [1–3], our understanding of two-atom systems is already conceptually comparable to the quantum-defect theory (QDT) of atomic Rydberg spectra [4]. Namely, the slow atomic scattering and the rovibrational spectrum of a particular angular momentum can be understood in terms of the long-range solutions and a parameter that is a slowly varying function of energy in the threshold region [5–7,1–3]. In this work, we show that a two-atom system possesses an even greater degree of systematics in the following sense. Unlike the QDT for atomic Rydberg spectra in which different angular-momentum states have different quantum defects with no general relationships among them, a single parameter is sufficient to characterize slow atomic collisions for practically all angular momenta. The same parameter also characterizes the rovibrational spectra in the threshold region, including states of different angular momenta. In other words, in addition to the relationship between the bound spectrum and scattering, as expected from traditional QDT formulations [4], a two-atom system has also the unique property that scattering of different angular momenta are related, and so are the bound spectra of different angular momenta.

The origin of this relationship between different angular-momentum states is not difficult to understand and is due to a combination of the following three properties of a typical molecular system. (i) Atoms are strongly repulsive at short distances. (ii) Atoms are heavy compared to electrons. (iii) The atom-atom interaction at large distances behaves as $1/r^n$ with $n>2$. The combination of the first two properties gives rise to the well-known separation of tightly bound rovibrational states into the product of two parts $\psi_v\psi_r$, in which the vibrational wave function ψ_v is, to the lowest order, independent of rotational quantum numbers. For rovibrational states that are highly excited, the same properties ensure that the radial wave function, up to a normalization constant, remains nearly independent of angular momentum until a distance is reached where the rotational energy term becomes comparable to the electronic and other energy terms. This characteristic is uniquely molecular and does not apply to the electronic wave functions of an atom, for which the rotational term dominates the behavior at sufficiently small r.

The implication of the third property can be understood from qualitative behaviors of the potential $-C_n/r^n+\hbar^2 l(l+1)/(2\mu r^2)$. For $n>2$ and $l\neq 0$, it has a maximum and crosses zero at $r_x=[l(l+1)]^{-1/(n-2)}\beta_n$, where β_n is a length scale associated with the $-C_n/r^n$ interaction as defined by

$$\beta_n \equiv (2\mu C_n/\hbar^2)^{1/(n-2)}. \tag{1}$$

From a physical point of view, r_x specifies the location at which the centrifugal potential is equal to the long-range interaction. For an l that is not too large, r_x is of the order of β_n. Since n is greater than 2, for distances that are smaller than r_x, the long-range interaction quickly dominates, and correspondingly, the importance of the angular momentum quickly diminishes. Mathematically speaking, this means that for a potential that goes to zero faster than $1/r^2$ at large distances, a pair of linearly independent solutions exist, which, at relatively small distances, are not only independent of energy, but also independent of angular momentum.

The combination of these characteristics leads to the following important conclusion. With a proper choice of long-range solutions, a quantum-defect theory for molecular rovibrational states and slow atomic collisions can be formulated in which the short-range parameters are not only nearly independent of energy, but also nearly independent of the relative angular momentum.

For a single channel with an asymptotic van der Waals interaction $(-C_6/r^6)$, the proper pair of long-range solutions are ones with the behavior

$$f^c_{\epsilon l} \overset{r\ll\beta_6}{\longrightarrow} (2/\pi)^{1/2}(r/\beta_6)r^{1/2}\cos(y-\pi/4), \tag{2}$$

$$g^c_{\epsilon l} \overset{r\ll\beta_6}{\longrightarrow} -(2/\pi)^{1/2}(r/\beta_6)r^{1/2}\sin(y-\pi/4), \tag{3}$$

for both positive and negative energies. Here $y=(r/\beta_6)^{-2}/2$. This pair, which has not only energy-independent, but also angular-momentum-independent be-

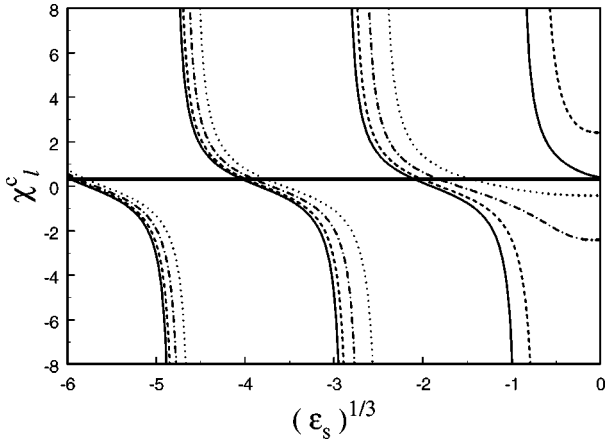

FIG. 1. The χ_l^c functions (dimensionless) for an attractive $1/r^6$ interaction plotted vs $(\epsilon_s)^{1/3}$ (dimensionless). Solid line, $l=0$; dashed line, $l=1$; dash-dotted line, $l=2$; dotted line, $l=3$. The bound spectra of any potential with $V(r)\rightarrow -C_6/r^6$ at large distances is given by the crossing points of this *same* set of functions with a set of system-specific $K^c(\epsilon,l)$. For systems that satisfy $\beta_6 \gg r_0$, $K^c(\epsilon,l)$ is approximately an *l-independent* constant in the threshold region, represented by a single horizontal line.

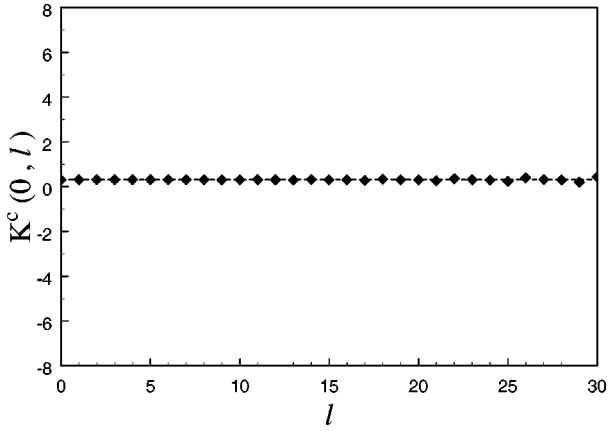

FIG. 2. Analytic results of $K^c(0,l)$, dimensionless and represented by black diamonds, vs l for a potential $V(r)=-C_6/r^6+C_{10}/r^{10}$ with $\beta_6/\beta_{10}=4.19\,186\,886$. The dashed horizontal line represents the constant $K^c=0.3106$.

havior at small distances, is related to the f^0 and g^0 pair defined in [1] by a linear transformation. In particular, they are given at zero energy by

$$f^c_{\epsilon=0l}=[2^{3/2}\cos(\pi\nu_0/2)]^{-1}r^{1/2}[J_{\nu_0}(y)+J_{-\nu_0}(y)], \quad (4)$$

$$g^c_{\epsilon=0l}=-[2^{3/2}\sin(\pi\nu_0/2)]^{-1}r^{1/2}[J_{\nu_0}(y)-J_{-\nu_0}(y)], \quad (5)$$

where $\nu_0=(l+1/2)/2$.

With this choice of long-range solutions, the single-channel quantum-defect theory is still formally the same as discussed previously [5,2,3]. In particular, the bound spectrum of any potential with the behavior of $V(r)\rightarrow -C_6/r^6$ at large distances is still given rigorously by the crossing points between a χ function, determined by the long-range solutions, and a short-range K matrix [5,3] (see Fig. 1)

$$\chi_l^c(\epsilon_s)=K^c(\epsilon,l). \quad (6)$$

Here χ_l^c corresponds to the choice of long-range solutions as specified by Eqs. (2) and (3). It is a function of a scaled bound-state energy ϵ_s defined by

$$\epsilon_s=\epsilon/[16(\hbar^2/2\mu)(1/\beta_6)^2], \quad (7)$$

and is given explicitly by

$$\chi_l^c=\frac{(Y_{\epsilon l}/X_{\epsilon l})+\tan(\pi\nu/2)(1+M_{\epsilon l})/(1-M_{\epsilon l})}{1-(Y_{\epsilon l}/X_{\epsilon l})\tan(\pi\nu/2)(1+M_{\epsilon l})/(1-M_{\epsilon l})}, \quad (8)$$

in which $M_{\epsilon l}=G_{\epsilon l}(-\nu)/G_{\epsilon l}(\nu)$, with ν, $X_{\epsilon l}$, $Y_{\epsilon l}$, and $G_{\epsilon l}$ being defined in [1]. K^c is a short-range K matrix that results from the matching of the short-range solution and the long-range solution. It is given explicitly by

$$K^c(\epsilon,l)=\left(\frac{f^c_{\epsilon l}}{g^c_{\epsilon l}}\right)\frac{(f^c_{\epsilon l}{}'/f^c_{\epsilon l})-(u_{\epsilon l}{}'/u_{\epsilon l})}{(g^c_{\epsilon l}{}'/g^c_{\epsilon l})-(u_{\epsilon l}{}'/u_{\epsilon l})}, \quad (9)$$

evaluated at any radius beyond r_0 at which the potential has become well represented by $-C_6/r^6$.

Above the threshold, the scattering K matrix is given by a similar expression as derived previously [5,2,3]:

$$K_l\equiv\tan\delta_l=(K^cZ^c_{gg}-Z^c_{fg})(Z^c_{ff}-K^cZ^c_{gf})^{-1}, \quad (10)$$

with the Z^c matrix as given in [8]. The key difference between the present formulation and the previous one is the following. With the choice of long-range solution pair as specified by Eqs. (2) and (3), and the property of the wave function discussed earlier, the parameter K^c is, under the condition of $\beta_n \gg r_0$ [5,2,3], not only independent of energy, but also independent of angular momentum l in the threshold region.

The degree to which K^c is independent of l can be estimated through an effective potential method. Specifically, we can easily design a potential, of the class of $LJ(n,2n-2)$: $V(r)=-C_n/r^n+C_{2n-2}/r^{2n-2}$, for which $K^c(0,l)$ can be found analytically [9], to support the same number of bound states and to have the same K^c for a particular l as the system of interest. The analytic $K^c(0,l)$ for the corresponding effective potential then gives a good indication of the l dependence of K^c for the desired system [10]. Figure 2 shows the l dependence of K^c for an Lennard-Jones (6,10) potential with $\beta_6/\beta_{10}=4.191\,868\,86$. This ratio has been chosen such that the corresponding potential supports 38 bound s states, same as that for the triplet state of $^{85}Rb_2$ [11], and has a $K^c(0,l=2)=0.3106$, equal to the value we will determine later in the article from experimental data. It shows that K^c has very little l dependence for a wide range of $0\leqslant l\leqslant 30$. This figure has been plotted on the same y scale as that of χ_l^c in Fig. 1 so that one can see clearly how insignificant the variations in K^c are. (The method of how to effectively design such a potential will be discussed in much more detail elsewhere [9].)

In addition to this method of effective potential, the degree to which K^c is independent of l can also be determined through a relationship between the energy independence and the l independence. They are related since they both rely on the wave function becoming a linear combination of the right-hand sides of Eqs. (2) and (3) before the potential starts to differ substantially from $-C_6/r^6$. An l expansion of Eq. (9) at zero energy shows that the l-dependent terms come in with a relative magnitude of $(l+1/2)^2/[4(\beta_6/r_0)^2]$. An expansion in energy shows that the energy-dependent terms come in with a relative magnitude of $\epsilon_s/[2(\beta_6/r_0)^2]$. The combination of the two leads to the following criterion. If K^c is independent of the (scaled) energy in a region of $|\Delta\epsilon_s|$ around the threshold, it will be, to the same degree of accuracy, independent of l for all l satisfying $(l+1/2)^2 \leqslant 2|\Delta\epsilon_s|$. This criterion has also a clear physical interpretation. Namely, if K^c is independent of energy in a region of $|\Delta\epsilon|$ around the threshold, it will be independent of l until the rotational energy, which has an order of magnitude of $8(\hbar^2/2\mu)(1/\beta_6)^2(l+1/2)^2$ around the threshold, becomes comparable to or greater than $|\Delta\epsilon|$. In the example of $^{85}Rb_2$, an energy independence of K^c over a range of 10 GHz (to be determined later) translates into an l independence up to $l \sim 30$, consistent with the effective potential results shown in Fig. 1. This l independence of K^c over a large range of l is due both to the smallness of the rotational energy around the threshold and to the fact that the same K^c describes multiple vibrational states near the threshold (energy independence).

The determination of the parameter K^c is, in principle, straightforward theoretically. It can be done, for example, by solving the radial equation at a small energy (include zero energy) and matching it to the proper long-range solution. However, since our present knowledge about both the short-range interaction and the C_n coefficients is still not sufficiently accurate for many systems, we focus here on the direct experimental determination of both the K^c parameter and the C_n coefficient. In particular, we show that if the C_n coefficient that characterizes the dominant long-range interaction is known accurately, the parameter K^c can be obtained from the measurement of a single binding energy (similar to the determination of K_l^0 discussed previously [5]). If binding energies of more than one state are known, in addition to the prediction of the parameter K^c, an accurate determination of C_n can also be made, especially when the two states are closely spaced in energy.

In Table I, the first column represents the experimental results [12] for states of $^{85}Rb_2$ characterized by quantum numbers $F_1=3$, $F_2=3$, $F=6$, $l=2$, and $T=8$ [13,14]. The results in the column labeled Theory II represents a simple calculation making use of only a single experimental energy. In this calculation, the energy of the level labeled $v_{max}-v=1$ in Table I is first scaled according to Eqs. (7) and (1) with $\mu=77\,392.368$ a.u. and a value of $C_6=4426$ a.u. from the theoretical calculation of Marinescu *et al.* [15]. The parameter K^c is determined by evaluating the $\chi^c_{l=2}$ function at this scaled energy [5], which yields a value of $K^c=0.2841$. The crossing points of this constant with $\chi^c_{l=2}(\epsilon_s)$ give the predictions of the other energy levels listed in this column

TABLE I. Comparison of energies, in GHz, of the last four bound states of $^{85}Rb_2$ characterized by quantum numbers $F_1=3, F_2=3, F=6, l=2, T=8$.

$v_{max}-v$	Experiment [a]	Theory I [b]	Theory II [c]	Theory III [d]
0	-0.16 ± 0.03	-0.15	-0.1513	-0.1539
1	-1.52 ± 0.03	-1.50	-1.520	-1.520
2	-5.20 ± 0.03	-5.16	-5.222	-5.200
3	-12.22 ± 0.06	-12.21	-12.37	-12.30

[a]From [12].
[b]From [12].
[c]$C_6=4426$ a.u. and $K^c=0.2841$.
[d]$C_6=4533$ a.u. and $K^c=0.3106$.

(see Fig. 1). Note that this simple calculation already yields excellent agreement with experiment and compares very favorably with a much more complex numerical calculation [12] listed under Theory I in Table I. This excellent agreement shows that the parameter K^c is indeed, to a very good approximation, a constant in the energy range covered by the experiment ($\sim$10 GHz). This is further confirmed by the fact that enforcing K^c to be constant leads to an even better agreement, a procedure that also demonstrates a method for the experimental determination of the leading C_n coefficient from a minimum of only two binding-energy measurements.

Keeping in mind that the C_6 value used in the first calculation is not necessarily the true C_6, it is allowed to vary in the following calculation. With more than one experimental binding energy available, we vary C_6 in such a way that the two χ^c_l evaluated at the two different scaled energies (they may also correspond to different l) are the same. In other words, we force the parameter K^c to be a constant. The refined C_6 is then given by the root of the following equation:

$$\chi^c_l(\epsilon_{s1})-\chi^c_{l'}(\epsilon_{s2})=0, \tag{11}$$

where ϵ_{s1} and ϵ_{s2} are two experimental energies scaled according to Eqs. (7) and (1) for van der Waals interactions. The reduced masses are known with great precision from atomic masses so that the only unknown on the left-hand side is the C_6 coefficient. This procedure, when applied to the two d states labeled in Table I $v_{max}-v=1$ and 2, respectively, leads to a revised $C_6=4533$ a.u., which is in good agreement with $C_6=4550\pm100$ a.u., determined by Boesten *et al.* [11]. This C_6 value refines the energy scaling and leads to a revised value of $K^c(0,l=2)=0.3106$. The column in Table I labeled Theory III gives the results of energy levels predicted using this set of revised parameters, and an even better agreement with experiment is achieved. This procedure demonstrates a method for the determination of the C_n coefficient from two or more values of experimental binding energies. It requires no knowledge of the short-range interactions, nor does it require numerical solutions of the Schrödinger equation. The closer in energy those two states are, the better this method works.

Since the parameter K^c is, to a very good approximation, independent of l, it can be used to predict the bound spectra of other angular momenta in the threshold region (see Fig.

TABLE II. Bound-state energies (in GHz) of $^{85}Rb_2$ with quantum numbers $F_1=3, F_2=3, F=6, l, T=F+l$ with $l=0,2,4,6$, respectively. They are predicted using $C_6=4533$ a.u. and $K^c=0.3106$.

$l=0$	$l=2$	$l=4$	$l=6$
−0.2341	−0.1539		
−1.678	−1.520	−1.161	−0.6244
−5.434	−5.200	−4.659	−3.826
−12.61	−12.30	−11.58	−10.46
−24.30	−23.91	−23.01	−21.61

1). Table II gives the predictions of the bound spectra of $^{85}Rb_2$ characterized by quantum numbers $F_1=3, F_2=3, F=6, l, T=F+l$, with $l=0,2,4,6$, respectively [13].

The fact that K^c is nearly a constant in the threshold region, in both ϵ and l, has the following important implications. (i) It provides an experimental verification of the breakdown of the large-quantum-number formulation of the correspondence principle, as a constant K^c in ϵ leads immediately to the spectral characteristics discussed in [3]. (ii) Since 1 GHz corresponds to 47.99 mK, the fact that K^c is independent of energy over a range of 10 GHz below the threshold implies that the same constant K^c can describe collisions over hundreds of millikelvins above the threshold, including states of different angular momenta and their associated shape resonances. Figure 3 shows the partial scattering cross sections for *s*, *d*, and *g* waves predicted by the same short-range parameter $K^c=0.3106$ for two doubly spin-polarized ^{85}Rb atoms. Only a small energy range is shown here to make for easy identification of the narrow *g* wave shape resonance [11]. (iii) Since the hyperfine splitting is typically of the order of 1 GHz, it means that the frame-transformation method for atom-atom scattering [14,6], when properly formulated with K^c being the short-range parameter [9], will work well in a multichannel formulation that includes hyperfine structures [14,6,7]. (iii) To the extent of K^c being ϵ- and l-independent, potentials with the same K^c have, with a proper scaling of energy, the same bound spectra and scattering properties around the threshold, including states of different angular momenta. This is a foundation for the concept of effective potential [9].

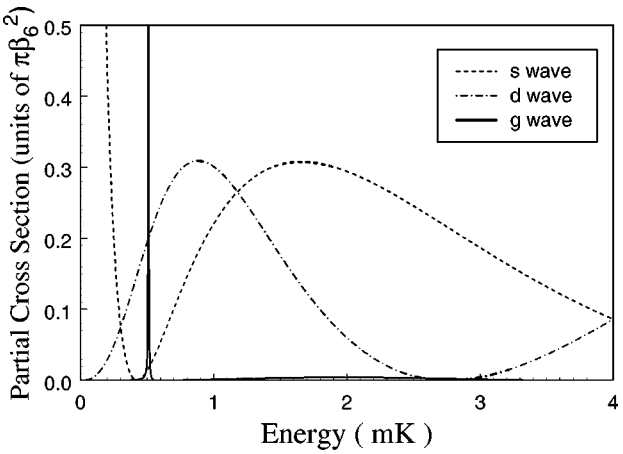

FIG. 3. Partial scattering cross sections for a pair of spin-polarized ^{85}Rb atoms in state $F_1=3$, $M_{F1}=3$, $F_2=3$, and $M_{F2}=3$. $\beta_6=162.7$ a.u. is determined with $\mu=77\,392.368$ a.u. and $C_6=4533$.

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