Universal Properties in Ultracold Ion-Atom Interactions

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We present some of the universal properties in ion-atom interaction derived from a newly formulated quantum-defect theory for the $-1/r^4$ type of long-range interactions. For bound states, we present the universal bound spectrum, namely, the equivalent of the Rydberg formula, for ion-atom systems. For scattering, we introduce the concept of a universal resonance spectrum to give a systematic understanding of many resonances present in ion-atom scattering. The theory further provides a method for an accurate spectroscopic determination of the atomic polarizability. It also suggests the existence of atomlike molecules, in which multiple atoms orbit around a heavy ion.

As experimental techniques for preparing and manipulating cold atomic ions improve [1], there is a rapidly growing interest in ion-atom interactions at ultracold temperatures [2–5]. While it is intuitively clear that an ion can exert a much stronger influence on its environment than either an atom or a molecule, the precise nature of this influence, especially at the quantum level, is far from being understood. For example, an ion-atom system is one of the few types of two-body systems for which their loosely bound states, namely, the highly excited rovibrational states right below the dissociation limit, are yet to be observed experimentally or fully characterized theoretically [6].

This work presents part of a newly formulated quantum-defect theory (QDT) for ion-atom interactions. It gives precise explanation and characterization of the meaning and the consequence of the "strong influence" of an ion on a neighboring atom. On a more technical level, it is a version of the QDT for $-1/r^4$ type of long-range potential [7–9] that brings our understanding of ion-atom interactions to the same level as, and in certain areas exceeding, our current understanding of ultracold atom-atom interactions [10]. The theory is a result of combining conceptual developments, built further upon Refs. [11–13], with improved mathematical understanding of the modified Mathieu functions [14–16], especially for negative energies. The latter development, which allows for the efficient determination of all QDT functions for $-1/r^4$ potential, is achieved by solving the modified Mathieu equation using techniques we have previously developed for the analytic solutions of $1/r^6$ [17] and $1/r^3$ [18] potentials.

We focus here on the universal spectrum for ion-atom interactions. For bound states, it is the equivalent of the Rydberg formula for $-1/r^4$ type of long-range potential, formulated in a way to take advantage of the angular momentum insensitivity of the short-range parameter that is a characteristic of atom-atom and ion-atom interactions [11,13,19]. It allows for the determination of the entire rovibrational spectrum in the threshold region from a single short-range parameter, such as the quantum defect. More importantly, the concept of universal spectrum is generalized here to positive energies to include scattering resonance positions. It facilitates a systematic understanding of many resonances that are present in ion-atom scattering [2,4,5], within the same framework, and using the same short-range parameter, as the bound spectrum. A number of more specific results will be extracted out of the universal spectrum, including the energy bins [10,12] that contain various loosely bound states or scattering resonances. Furthermore, we show that there exists a critical energy, below which all scattering resonances have positive widths that correspond to time delay [20], and above which all scattering resonances have negative widths that correspond to time advance [20]. Such concepts, together with the concept of universal width function to be briefly discussed there, provide what we believe to be the first systematic understanding of the global structure of scattering. Conceptually, they are expected to be generally applicable to all quantum systems with $-1/r^n$ type of long-range potential with $n > 2$. We briefly outline selective qualitative features of ion-atom interaction before getting to the mathematical formulation and the results of the theory.

Like other quantum systems around the threshold, ion-atom interaction in the ultracold regime is determined primarily by its long-range interaction. Assuming that the atom involved has no permanent quadrupole, such as the case for alkali-metal atoms in their ground states, the long-range ion-atom interaction has the form of $V(r) \sim -C_4/r^4$ where C_4 is related, in atomic units, to the static dipole polarizability of the atom, α_1, by $C_4 = \alpha_1/2$. The qualitative features of ion-atom interaction can be understood through the length scale, $\beta_4 = (2\mu C_4/\hbar^2)^{1/2}$, and other related scale parameters that are associated with the long-range potential. Table I gives samples of such parameters for alkali-metal systems. The length scale β_4 is a measure of the size of the last few loosely bound states. The corresponding energy scale, $s_E = (\hbar^2/2\mu)(1/\beta_4)^2$, sets the scale for their energy spacing. The related time scale $s_T = \hbar/s_E$ sets the scale for, e.g., the lifetime of a shape reso-

TABLE I. Sample scale parameters for ion-atom systems. C_4, in atomic units, is given by $\alpha_1/2$ where α_1 is the static dipole polarizability of the atom. The $\beta_4 = (2\mu C_4/\hbar^2)^{1/2}$ is the length scale. The $s_E = (\hbar^2/2\mu)(1/\beta_4)^2$ is the corresponding energy scale. It is given both in units of microkelvin and in units of kHz.

System	C_4 (a.u.)	β_4 (a.u.)	s_E/k_B (μK)	s_E/h (kHz)
^{87}Rb$^+$ $-$ ^{6}Li	82.06[a]	1297	9.148	190.6
^{87}Rb$^+$ $-$ ^{23}Na	81.30[b]	2321	0.8841	18.42
^{6}Li$^+$ $-$ ^{6}Li	82.06[a]	948.5	32.01	667.0
^{23}Na$^+$ $-$ ^{23}Na	81.30[b]	1846	2.212	46.08
^{40}K$^+$ $-$ ^{40}K	145.1[b]	3251	0.4101	8.545
^{133}Cs$^+$ $-$ ^{133}Cs	199.9[b]	6959	0.026 91	0.5608

[a]Using α_1 from Ref. [21].
[b]Using α_1 from Ref. [22].

nance, and $\pi\beta_4^2$ sets the scale for low-energy scattering cross section.

A large length scale β_4 is what characterizes the "strong influence" of an ion on its environment. From Table I, it is clear that ion-atom interaction has a much longer length scale than either the atom-atom interaction, with a corresponding length scale of $\beta_6 \sim 100$ a.u., or the electron-atom interaction, with a corresponding length scale of $\beta_4 \sim 10$ a.u. More importantly, the β_4 for ion-atom is hundreds times greater than r_0, the distance below which the ion-atom interaction starts to deviate from the $-C_4/r^4$ behavior, and which can be estimated to be of the order of $r_0 \sim 10$–30 a.u.. The implication of this large scale separation is that an ion-atom system typically supports thousands of bound states, and, from Levinson theorem [23], thousands of scattering resonances, with many of them around the threshold following the universal behavior as described by the angular-momentum-insensitive formulation of the quantum-defect theory (AQDT) [11,13].

Universal bound spectrum.—In AQDT [11,13], the bound spectrum of a two-body system with $-1/r^n$ ($n > 2$) type of long-range potential is given rigorously by the solutions of

$$\chi_l^{c(n)}(\epsilon_s) = K^c(\epsilon, l). \tag{1}$$

Here the $\chi_l^{c(n)}$ function is a universal function of a scaled energy, $\epsilon_s = \epsilon/s_E$, that is uniquely determined by the exponent of the long-range interaction n and the angular momentum l. All the short-range physics is encapsulated in the parameter $K^c(\epsilon, l)$. It is a short-range K matrix that is a meromorphic function of both ϵ and l [13]. The K^c parameter is further related to the quantum defect μ^c, which is defined to have a range of $0 \le \mu^c < 1$, by $K^c(\epsilon, l) = \tan[\pi\mu^c(\epsilon, l) + \pi b/2]$ where $b = 1/(n-2)$ [13].

For $n = 4$, we have obtained all QDT functions of Ref. [13] through an improved understanding of the modified Mathieu equation [14–16]. In particular, we have obtained the universal $\chi_l^{c(n)}$ function for $n = 4$:

$$\chi_l^{c(4)} = \tan(\pi\nu/2)\frac{1 + M_{\epsilon_s l}^2}{1 - M_{\epsilon_s l}^2}, \tag{2}$$

where ν is the characteristic exponent for $-1/r^4$ type of potential [14–16,24], and

$$M_{\epsilon_s l}(\nu) = 2^{-2\nu}|\epsilon_s|^{\nu/2}\left(\frac{\Gamma[1 - (\nu + \nu_0)/2]}{\Gamma[1 + (\nu + \nu_0)/2)]}\right)$$
$$\times \left(\frac{\Gamma[1 - (\nu - \nu_0)/2]}{\Gamma[1 + (\nu - \nu_0)/2]}\right)\left(\frac{C_{\epsilon_s l}(-\nu)}{C_{\epsilon_s l}(+\nu)}\right), \tag{3}$$

in which $\nu_0 = l + 1/2$,

$$C_{\epsilon_s l}(\nu) = \prod_{j=0}^{\infty} Q(\nu + 2j), \tag{4}$$

with $Q(\nu)$ being given by a continued fraction

$$Q(\nu) = \cfrac{1}{1 - \cfrac{\epsilon_s}{[(\nu+2)^2 - \nu_0^2][(\nu+4)^2 - \nu_0^2]}Q(\nu + 2)}. \tag{5}$$

Equations (1) and (2) give the universal bound spectrum for $-1/r^4$ type of long-range interaction. Figure 1 gives one of its possible graphical representations, in combination with the universal resonance spectrum to be discussed next.

Universal scattering properties.—In AQDT, the single-channel scattering properties are determined from [13]

$$K_l \equiv \tan\delta_l = (Z_{gc}^{c(n)}K^c - Z_{fc}^{c(n)})(Z_{fs}^{c(n)} - Z_{gs}^{c(n)}K^c)^{-1}, \tag{6}$$

where $Z_{xy}^{c(n)}(\epsilon_s, l)$ are again universal QDT functions that are uniquely determined by the long-range exponent n and the angular momentum l [13].
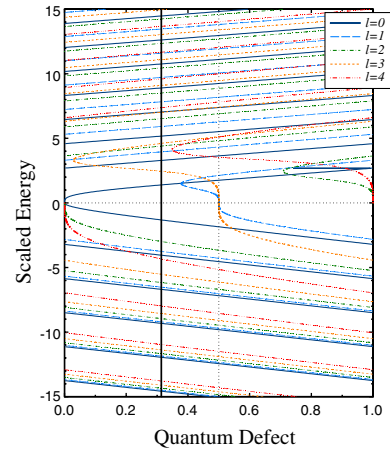

FIG. 1 (color online). The universal spectrum for two-body quantum systems with $-1/r^4$ type of interactions, including both the universal bound spectrum for $\epsilon < 0$, where the y-axis is defined as $-(-\epsilon_s)^{1/4}$, and the universal resonance spectrum for $\epsilon > 0$, where the y-axis is defined as $(\epsilon_s)^{1/4}$. For any two-body quantum system with $-1/r^4$ type of long-range potential, the bound spectrum and the resonance spectrum are given by the cross points between the curves plotted and the curves representing $\mu^c(\epsilon, l)$. For systems such as ion-atom, for which $\beta_4 \gg r_0$, $\mu^c(\epsilon, l)$ is approximately an l-independent constant, allowing the determination of the entire rovibrational spectrum, and the resonance spectrum, from a single parameter, as illustrated by a vertical line in the figure.

We use here the definition of scattering resonance positions as energies at which $\sin^2 \delta_l = 1$, namely, the energies at which the scattering cross section reaches its unitarity limit [24]. Such locations can be determined as the roots of the denominator in Eq. (6). Defining a generalized $\chi_l^{c(n)}$ function for positive energies as $\tilde{\chi}_l^{c(n)}(\epsilon_s) \equiv Z_{fs}^{c(n)}/Z_{gs}^{c(n)}$, the resonance positions can be formulated in a similar fashion as the bound spectrum, as the solutions of

$$\tilde{\chi}_l^{c(n)}(\epsilon_s) = K^c(\epsilon, l). \tag{7}$$

For $n = 4$, we have obtained

$$\tilde{\chi}_l^{c(4)} = \tan(\pi\nu/2)\frac{1 - (-1)^l M_{\epsilon_s l}^2 \tan[\pi(\nu - \nu_0)/2]}{1 + (-1)^l M_{\epsilon_s l}^2 \tan[\pi(\nu - \nu_0)/2]}, \tag{8}$$

in which ν, ν_0, and $M_{\epsilon_s l}$ are the same as those defined earlier in relation to the bound spectrum.

Equations (7) and (8) give the universal resonance spectrum for $-1/r^4$ type of long-range interaction. The $\epsilon > 0$ portion of Fig. 1 gives one of its possible graphical representations. Similar to a bound spectrum, which describes, over a set of discrete energies, the rise of a phase from zero to a finite value at the threshold, a resonance spectrum describes its subsequent evolution back towards zero. For a scattering resonance located at ϵ_{sl}, which is one of the solutions of Eq. (7), the width of the resonance, again derived from Eq. (6), is given by

$$\gamma_l(\epsilon_{sl}) = -2\left\{\frac{d\tilde{\chi}_l^{c(n)}}{d\epsilon_s}\bigg|_{\epsilon_{sl}} [Z_{gs}^{c(n)}(\epsilon_{sl}, l)]^2\right\}^{-1}. \tag{9}$$

It shows that while the position of a scattering resonance depends on the short-range parameter, the width of the resonance, as a function of the resonance position, follows a universal behavior that is uniquely determined by the long-range interaction. We call Eq. (9) the universal width function.

There are a number of conclusions that can be drawn from the universal spectrum. We give here a brief summary, with more complete discussions to be given elsewhere. (i) For ion-atom systems, namely, systems with $\beta_4 \gg r_0$, the universal spectrum allows the determination of the entire rovibrational spectrum and the entire resonance spectrum in the threshold region, including states of different l, using a single parameter, assuming α_1 is known accurately. This single parameter can be determined from the measurement of either a single bound state energy [11], or a single resonance position. (ii) From measurements of two or more bound state energies and/or resonance positions, and using the method of Ref. [11] and its generalizations, the universal spectrum can give not only an accurate prediction of the entire spectrum, but also an accurate, spectroscopic determination of the atomic dipole polarizability, with no knowledge required of the details of the atomic interaction at short distances [11]. The accuracy that can be expected with such a measurement is conservatively estimated to be 10^{-6}, far better than the best achieved using atomic interferometry [25]. (iii) The measurements of bound state energies and resonance positions are further facilitated by the energy bin concept [10,12] embedded in the universal spectrum. They give ranges of energies in which a certain state is to be found, as explained and tabulated in Table II and illustrated in Fig. 2. The earlier version of the concept [10,12] has been generalized here to include bins for resonance states. (iv) The properties of the $\tilde{\chi}_l^c$ functions show that there exists a critical energy for each l, $B_c(l)$, defined by $d\tilde{\chi}_l^{c(n)}/d\epsilon_s|_{B_c(l)} = 0$. Below $B_c(l)$, $\tilde{\chi}_l^{c(n)}$ is a piecewise monotonically decreasing function of energy with $d\tilde{\chi}_l^{c(n)}/d\epsilon_s < 0$, which, from Eq. (9), implies that all resonances occurring in this region have positive widths corresponding to time delays [20]. Above $B_c(l)$, $\tilde{\chi}_l^{c(n)}$ evolves into a piecewise monotonically increasing function of energy with $d\tilde{\chi}_l^{c(n)}/d\epsilon_s > 0$, implying that all resonances above $B_c(l)$ have negative widths

TABLE II. Energy bins for the first few partial waves. The ith bound state of angular momentum l, with $i = 1$ corresponding to the least-bound state, is to be found within $B_{-i} \le \epsilon_s < B_{-i+1}$ for $i > 1$, and within $B_{-1} \le \epsilon_s < 0$ for $i = 1$. Shape resonances of angular momentum l can only exist between $0 < \epsilon_s < B_c$. The ith diffraction resonance of angular momentum l, defined as a resonance with negative width, is to be found within $B_{i-1} < \epsilon_s \le B_i$ for $i \ge 1$. A zeroth diffraction resonance may exist within $B_c < \epsilon_s \le B_0$, depending on the quantum defect.

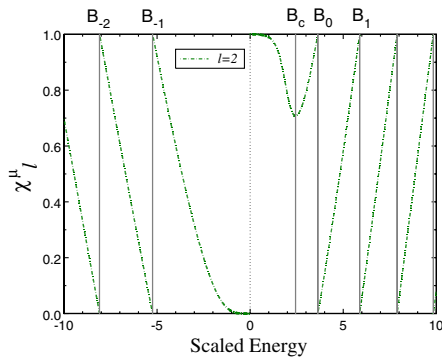| B_x	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$
B_4	4782.3	10 266	19 073	32 206	50 780
B_3	1734.9	4480.1	9371.7	17 218	28 940
B_2	442.02	1553.1	3886.6	8057.0	14 792
B_1	52.766	350.37	1199.8	3021.3	6348.0
B_0	0	20.514	174.75	687.38	1896.0
B_c	0	4.8878	35.505	120.16	292.38
B_{-1}	−105.81	−336.54	−753.97	−1407.4	−2345.8
B_{-2}	−1179.9	−2432.9	−4284.6	−6835.1	−10 184
B_{-3}	−5207.5	−8840.6	−13 708	−19 961	−27 750
B_{-4}	−15 308	−23 247	−33 279	−45 607	−60 433

FIG. 2 (color online). Illustrating definitions of energy bins, and the critical energy B_c, using the case d wave. The "scaled energy" is defined as in Fig. 1. The y axis is defined as $\chi_l^\mu = [\tan^{-1}(\chi_l^c) - \pi b/2]/\pi$, in which $\tan^{-1}(\chi_l^c)$ is taken to be within a range of π of $[\pi b/2, \pi + \pi b/2]$. Figure 1 is made up of multiple such curves for different l, except that they are turned around for a better visualization of the spectrum.

corresponding to time advances [20]. Such resonances will be called diffraction resonances [24] to distinguish them from shape resonances, which have positive widths. We note that the incorporation of diffraction resonances into the resonance spectrum is essential to complete the physical picture of the evolution of the phase back towards zero. (v) The universal spectrum gives the maximum number of shape resonances that can exist for a particular l. As can be observed from Fig. 1, this number is one for $l = 1$ through 4. Results for other l will be presented elsewhere, which show, e.g., that the minimum l that can support two shape resonances is $l = 7$ for ion-atom interactions. (vi) The results here provide explicit illustrations and confirmations of the general properties of $-1/r^n$ ($n > 2$) type of interactions derived earlier, such as the breakdown of the semiclassical approximation around the threshold (see Ref. [13] and the references therein), and the conclusion that the least-bound state for an ion-atom system is either an s state or a p state, depending on the quantum-defect [19]. (vii) The large size of an ion-atom bound state, as compared to the range of atom-atom interaction, implies that a heavy ion is likely to be able to bound multiple light atoms, especially in different vibrational states (orbits), in which atom-atom interactions are likely to be negligible. Such states, which can be expected to be much more stable than the states proposed by Côté *et al.* [3], are conceptually similar to the doubly or multiply excited states of an atom, except that the latter states have much shorter lifetimes due to strong electron-electron interactions. It will be interesting to find out how many atoms can be bound in such states, and how their properties depend on their configurations, and parameters such as the atom-ion mass ratio, atomic statistics, and atom-atom scattering characteristics.

In conclusion, we have shown that in addition to the more obvious aspect of having a large scattering cross section, the "strong influence" of an ion on a neighboring atom is reflected in the presence of a large number of bound states and scattering resonances around the threshold, a situation that would normally complicates its description. Fortunately, the very same strong influence, as characterized by a large β_4, simultaneously ensures that all such states follow universal properties determined solely by the long-range potential. Further studies of few-body and many-body systems involving ions will help to reveal their important roles in chemical reactions and in catalysis.

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