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Quantum-defect theory of atomic collisions and molecular vibration spectra

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A quantum-defect theory of atomic collisions and molecular vibration spectra is presented. Based on the exact solutions of the Schrödinger equation for an attractive $1/r^6$ potential, the theory provides a systematic interpretation of molecular bound states and atom-atom scattering properties and establishes the relationship between the two. Applications to systems including $^7\mathrm{Li}_2$ and $^{23}\mathrm{Na}_2$ are discussed. [S1050-2947(98)08611-9]

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Advances in laser and evaporative cooling and the realizations of Bose-Einstein condensation in cold atomic vapors [1] have stimulated a resurgence of theoretical interest in cold-atom collisions. Despite significant progress especially for alkali-metal atom systems [2–13], most of our present understandings tend to be system specific and numerically based. They do not yet provide significant insight about the general characteristics of cold atomic collisions.

Based on the exact solutions of the Schrödinger equation for an attractive $1/r^6$ potential, the details of which can be found elsewhere [14], we present here a quantum-defect theory (QDT) [15,16] that gives a general characterization of all diatomic systems that interacts asymptotically via an attractive $1/r^6$ potential. Specifically, in the case of a single channel, the bound energy levels of any potential, which is an attractive $1/r^6$ at long range, are formulated as the crossing points between a universal function of a scaled energy and an analytic function of energy that is determined by the short-range interactions only. Above the threshold, the theory provides a parametrization of energy dependencies of scattering phase shifts and cross sections that is more powerful than the traditional parametrization in terms of scattering length and effective range. It incorporates the energy dependencies induced by the long-range potential exactly, and is applicable not only to the *s* wave but also to the higher partial waves for which scattering length and/or effective range may not be defined. The theory further provides a relationship between bound and continuum properties and makes possible the predictions of scattering parameters, such as the scattering length and effective range, from experimental binding energies and the C_6 coefficient.

Consider a system of two atoms whose interaction beyond a distance of r_0 is represented accurately by an attractive $1/r^6$ potential. (Depending on the atoms involved, r_0 is typically 10–20 a.u.) With the exact solutions of the Schrödinger equation for the $1/r^6$ potential, the wave function at $r \geqslant r_0$ can always be written as

$$u_{\epsilon l}(r) = A_{\epsilon l}[f^0_{\epsilon l}(r) - K^0_l g^0_{\epsilon l}(r)], \tag{1}$$

where f^0 and g^0 are a pair of linearly independent solutions for the $1/r^6$ potential with energy-independent normalization near the origin [17]. With this choice of reference pair functions, the so-called short-range K matrix K^0, which is related to the logarithmic derivative of the wave function at or beyond r_0, is an analytic function of energy and is determined by the short-range interactions only [14].

From the asymptotic forms of f^0 and g^0 below the threshold,

$$f^0_{\epsilon l}(r) \xrightarrow{r\to\infty} (2\pi\kappa)^{-1/2}[W_{f-}e^{\kappa r} + W_{f+}e^{-\kappa r}], \tag{2}$$

$$g^0_{\epsilon l}(r) \xrightarrow{r\to\infty} (2\pi\kappa)^{-1/2}[W_{g-}e^{\kappa r} + W_{g+}e^{-\kappa r}], \tag{3}$$

where the W functions are discussed elsewhere [14], one can write the boundary condition for bound states, $u_{\epsilon l}(r\to\infty)\to 0$, as

$$\chi_l(\Delta) = K^0_l(\epsilon). \tag{4}$$

For a specific angular-momentum quantum number l, the function $\chi_l(\Delta) = W_{f-}/W_{g-}$ is a universal function of a scaled energy $\Delta \equiv (1/16)[\epsilon/(\hbar^2/2\mu)(1/\beta_6)^2]$, where β_6 is a length scale associated with the asymptotic $1/r^6$ potential and is defined in terms the C_6 coefficient by $\beta_6 \equiv (2\mu C_6/\hbar^2)^{1/4}$. The χ_l function is universal in the sense that it is the same for all potentials that are attractive $1/r^6$ at large distances, regardless of their behavior at short distances or the value of C_6 coefficient which only scales the energy differently. The χ_l function for $l=0$ is plotted in Fig. 1. Also

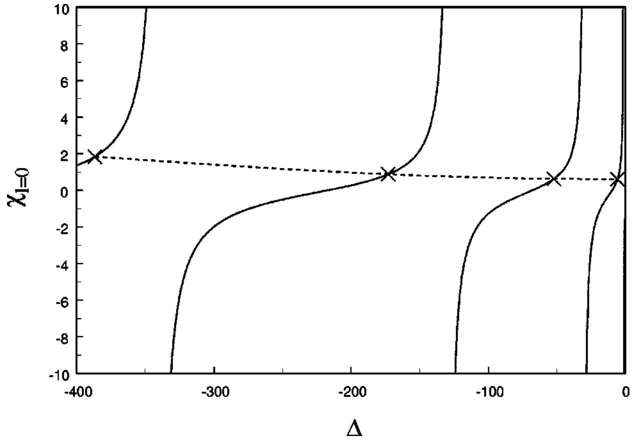

FIG. 1. The χ function for $l=0$. Also plotted is the discrete representation (the crosses) of $K^0_{l=0}$ for the $a^3\Sigma^+_u$ state of $^7\mathrm{Li}_2$.

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plotted, as an illustration, are the bound energy levels for the $a^3\Sigma_u^+$ state of $^7\mathrm{Li}_2$ as calculated by Cote *et al.* [5].

Above the threshold, the scattering phase shift can be written as

$$K_l \equiv \tan\delta_l = (K_l^0 Z_{gg} - Z_{fg})(Z_{ff} - K_l^0 Z_{gf})^{-1} \quad , \tag{5}$$

where the Z functions are again a set of universal functions of the scaled energy Δ, which characterizes the asymptotic behaviors of f^0 and g^0 above the threshold [14].

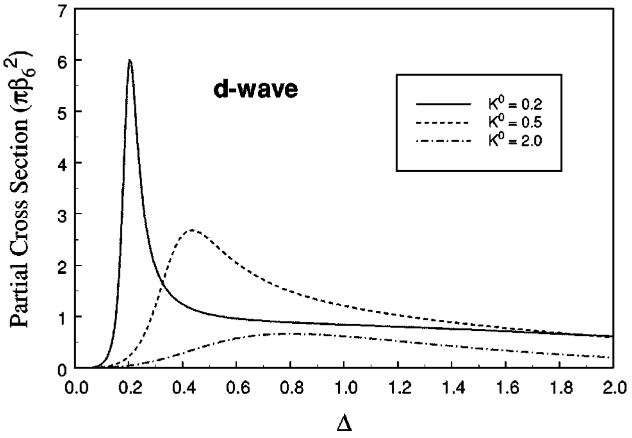

FIG. 2. The *d*-wave partial cross section as a function of the scaled energy.

The QDT formulation as represented by Eqs. (4) and (5) serves to separate the roles of short- and long-range interactions in both the bound-state spectra and the continuum scattering properties. This separation is useful for a number of reasons. First, for sufficiently large angular momentum, the scattering phase shift is determined almost exclusively by the long-range interaction. This will be reflected in the relative magnitudes of the Z functions in Eq. (5). Second, with this separation, K^0 is an analytic function of energy and can be easily parametrized and extrapolated across the threshold, thus establishing the relationship between bound spectra and continuum properties. Near the threshold, the χ and Z functions vary with energy on a scale of $(\hbar^2/2\mu)(1/\beta_6)^2$ while K^0 varies with energy on a scale of $(\hbar^2/2\mu)(1/r_0)^2$. The QDT formulation and the parametrization of K^0 are especially useful when the long-range interaction is strong such that $\beta_6 \gg r_0$, in which case the energy dependencies near the threshold are dominated by the long-range interaction for all l. Under this same condition, which is well satisfied by all alkali-metal atoms [18], the combination of $-C_6/r^6$ and the centrifugal potential $(l>0)$ forms a potential barrier at a large distance where the short-range interactions can be ignored. Since the shape of this barrier is determined solely by the long-range interaction, the propagation of the wave function through it and thus the shape of the shape resonance [12] is fully embedded in the Z functions, which come from the exact solution of Schrödinger equation for the attractive $1/r^6$ potential. Figure 2 illustrates the *d*-wave shape resonances for a sample of different K^0. Different atoms can have different K^0, which leads to different shapes of shape resonances. But they are all described by the same set of universal functions Z. Different C_6 coefficients only scale the energy differently. This is the only realistic potential barrier that we know where the shape resonances can now be described analytically.

Even though the Z functions can be calculated exactly [14], it is instructive to see the small Δ expansion of Eq. (5), which gives a simple analytic description of the energy dependencies of cold-atom collisions and relates the QDT description to the traditional scattering length–effective range description when these parameters can be defined. For small Δ, Eq. (5) gives

$$\begin{aligned}(k\beta_6)\cot\delta_{l=0} = -\{&K_{l=0}^0 + (1/3)(k\beta_6)^2 + (11/900)[K_{l=0}^0 - (30\pi/11)](k\beta_6)^4 - (2\pi^2/15)[\Gamma(1/4)]^{-2}(K_{l=0}^0 - 1)(k\beta_6)^5 \\ &+ (\pi/90)[K_{l=0}^0 - (181/70\pi)](k\beta_6)^6\}(2\pi[\Gamma(1/4)]^{-2}\{1 - (4/15)(k\beta_6)^4 \ln(k\beta_6) + (2/15)[(22/5) + \ln 2 - \gamma] \\ &\times (k\beta_6)^4\}\{(K_{l=0}^0 - 1) + (1/3)(K_{l=0}^0 + 1)(k\beta_6)^2 + (11/900)[(K_{l=0}^0 - 1) + (30\pi/11)(K_{l=0}^0 + 1)](k\beta_6)^4 \\ &- (\pi/90)[(K_{l=0}^0 - 1) + (181/70\pi)(K_{l=0}^0 + 1)](k\beta_6)^6\} - (\pi/15)[K_{l=0}^0 + (1/3)(k\beta_6)^2](k\beta_6)^3)^{-1}\end{aligned} \tag{6}$$

$$\begin{aligned}(k\beta_6)^3\cot\delta_{l=1} = [&K_{l=1}^0 - (1/5)(k\beta_6)^2]\{(\pi/18)[\Gamma(3/4)]^{-2}[(K_{l=1}^0 + 1) + (1/5)(K_{l=1}^0 - 1)(k\beta_6)^2] \\ &- (\pi/35)K_{l=1}^0(k\beta_6)\}^{-1},\end{aligned} \tag{7}$$

$$\tan\delta_{l\geqslant 2} = (3\pi/32)\{(l+1/2)[(l+1/2)^2 - 4][(l+1/2)^2 - 1]\}^{-1}(k\beta_6)^4. \tag{8}$$

Here γ is Euler's constant and K_l^0 is the short-range K matrix. These expansions of the phase shifts are such that the cross sections are determined consistently to the order of k^6, which corresponds to the lowest order at which all partial waves with $l \geqslant 2$ contributes. The result for $l \geqslant 2$ agrees with those of Levy and Keller [19]. For $l=0$ and $l=1$, which are the most important contributions to cold-atom collisions, their work does not offer closed equations for the phase shifts.

By comparing Eqs. (6)–(8) with the standard effective range expansion, one observes that for a $1/r^6$ potential, the scattering lengths have a definition only for s and p waves and the effective range has a definition only for the *s* wave [20]. In contrast, K_l^0 and Eq. (5) are well defined for all l. The *s*- and *p*-wave scattering lengths are related to $K_l^0(\epsilon)$ at $\epsilon=0$ by

$$a_{l=0}=\frac{2\pi}{[\Gamma(1/4)]^2}\frac{K_{l=0}^0(0)-1}{K_{l=0}^0(0)}\beta_6, \tag{9}$$

$$a_{l=1}=-\frac{\pi}{18[\Gamma(3/4)]^2}\frac{K_{l=1}^0(0)+1}{K_{l=1}^0(0)}\beta_6^3. \tag{10}$$

The *s*-wave effective range is related to $K_{l=0}^0$ and its derivative at $\epsilon=0$ by

$$r_{el=0}=\frac{[\Gamma(1/4)]^2}{3\pi}\frac{[K_{l=0}^0(0)]^2+1}{[K_{l=0}^0(0)-1]^2}\beta_6 + \frac{[\Gamma(1/4)]^2}{\pi}\frac{K_{l=0}^0{}'(0)(\hbar^2/2\mu)(1/\beta_6)^2}{[K_{l=0}^0(0)-1]^2}\beta_6. \tag{11}$$

Under the condition of $\beta \gg r_0$, satisfied by alkali-metal atoms [18], the variation of $K_{l=0}^0$ over an energy range of $(\hbar^2/2\mu)(1/\beta_6)^2$ is small and the second term in Eq. (11) can be neglected. In this case the *s*-wave scattering length and effective range are no longer independent but are related to each other through Eqs. (9) and (11). This relationship has been checked against independent numerical calculations by Cote *et al.* [5,6] for both singlets and triplets of $^7\mathrm{Li}_2$ and $^{23}\mathrm{Na}_2$ and excellent agreements have been found. For example, using a scattering length of 77.286 a.u. calculated by Cote and Dalgarno for the $a^3\Sigma_u^+$ state of $^{23}\mathrm{Na}_2$ [6], Eqs. (9) and (11) predict $r_e=62.378$ a.u., which is in excellent agreement with their result of 62 a.u. Note that it is only the consistency that we are checking here. If the more accurate value of scattering length, 85 a.u., determined by Tiesinga *et al.* [10] is used, Eqs. (9) and (11) predict an effective range of 61.8 a.u. Equation (11) further asserts that the *s*-wave effective range is positive for an attractive $1/r^6$ potential under the condition of $\beta_6 \gg r_0$ [18], which implies that a positive slope for the cross section at the threshold would correspond to a positive *s*-wave scattering length [21].

Equations (6)–(8) give a concise description of energy dependencies of cold-atom collisions. Other than an energy scaling factor, different atomic pairs differ from each other only in K^0, which can be easily parametrized especially under the condition of $\beta \gg r_0$. Figure 3 shows the elastic cross section for the collision between two ^{7}Li atoms spin polarized in state $|F=I+1/2, M_F=I+1/2\rangle$. Two parameters are used. First is the *s*-wave triplet scattering length determined by Abraham *et al.* [9], from which $K_{l=0}^0$ is obtained through Eq. (9). Second is C_6, which is taken from the calculation of Marinescu *et al.* [22]. Contributions from all even partial waves with $l \geq 2$ have been summed over analytically [14].

The quantum-defect theory presented here allows for the determination of atom-atom scattering properties, which are difficult to measure directly, from molecular binding energies that have the potential to be determined accurately by photoassociation spectroscopy [23,9,13]. The χ_l function evaluated at bound energy levels provides a discrete representation of $K_l^0(\epsilon)$ that can be extrapolated to the threshold and above to give the scattering properties. (Figure 1 illustrates this representation of $K_{l=0}^0$ for the $a^3\Sigma_u^+$ state of $^7\mathrm{Li}_2$ using the theoretical binding energies calculated by Cote *et al.* [5].) Specifically, from the known binding energies, we can calculate [cf. Eq. (4)]

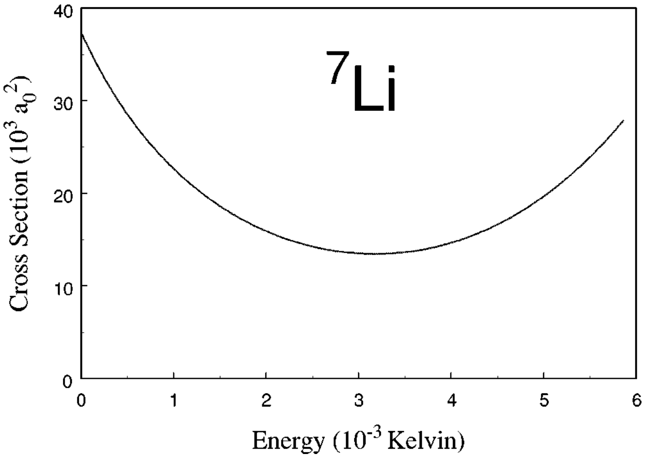

FIG. 3. Elastic scattering cross section between two spin-polarized ^{7}Li atoms.

$$K_l^0(\epsilon_i)=\chi_l(\Delta_i), \tag{12}$$

where the right-hand side is simply the values of the universal χ_l function evaluated at the (scaled) binding energies. Since K_l^0 is an analytic function of energy, it can be expanded as

$$K_l^0(\epsilon)=K_l^0(0)+\xi_1\epsilon+\xi_2\epsilon^2+\cdots. \tag{13}$$

The values of K_l^0 at the bound energies levels, $K_l^0(\epsilon_i)$, can thus be extrapolated to the threshold and above to give in particular $K_l^0(\epsilon=0)$, from which the scattering length and effective range can be determined from Eqs. (9) and (11). For $l \geq 1$, K_l^0 can also be determined by Eq. (5) from the position of a shape resonance [12].

As an example, for the $X^1\Sigma_g^+$ state of $^{23}\mathrm{Na}_2$, a constant extrapolation [meaning setting $\xi_1=\xi_2=0$ in Eq. (13)] using the binding energy of the least-bound state calculated by Cote and Dalgarno [6] gives us $a_0=35.1$ and $r_{e0}=184.9$, both of which are in excellent agreement with the results of their numerical calculation, which had a_0 in between 34.9 and 35.6 and r_{e0} in between 184 and 187.5. Again it is the consistency that matters here, i.e., when we use the binding energy calculated using the specific potential chosen by Cote and Dalgarno [6], we obtain the same scattering length and effective range as their numerical calculation. Only the binding energy of the least bound state (which could have come from an experimental measurement) and the C_6 coefficient [22] goes into our calculation.

For the $a^3\Sigma_u^+$ state of $^7\mathrm{Li}_2$, we obtain, using the experimental binding energy of the least-bound state as determined by Abraham *et al.* [9], an *s*-wave scattering length of $a_0=-30.3$ a.u., which is in good agreement with their result of

-27.3 a.u. The effective range predicted by Eqs. (9) and (11) is 530 a.u. if the value of $a_0=-27.3$ a.u. is used.

In conclusion, a quantum-defect theory for an attractive $1/r^6$ potential is presented. It provides a consistent parametrization of both the bound molecular vibrational states and the slow atomic collision cross sections, including states with $l\geqslant 2$ for which the scattering lengths are not defined. The theory serves as a foundation upon which more complete theories, which can be multichannel and include the corrections to the long-range $1/r^6$ potential, can be based.

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