A Two-State Model for Controlling Scattering Lengths and Photoassociation Spectral Line Shapes of Alkali-Metal Atoms by Resonant Light in the Regime of Finite Ultracold Temperature

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In this work we present, in a very didactic and careful way, a two-state model for binary collisions of alkali-metal atoms in the regime of finite ultracold temperature. We derive the modification of scattering lengths by nearly-resonant light and the shapes of photoassociation spectral lines from the same formalism. We emphasize the necessary approximations involved in this unified approach and treat the realistic case of a molecular transition electric-dipole moment that depends on the interatomic distance.

I. Introduction

The essential scheme of photoassociation spectroscopy, first proposed by Thorsheim, Weiner, and Julienne [1], and realized experimentally by several groups [2–13], is as follows. Two approaching ground-state atoms, of asymptotic relative kinetic energy E, absorb a photon of energy $\hbar\omega$ and associate as a molecular excited bound state $|b\rangle$ of energy E_b. Then, a product state $|p\rangle$ is detected, in which the bound state $|b\rangle$ manifests itself as a resonance satisfying $E_b = E + \hbar\omega$. As we scan the frequency ω of the exciting laser, we obtain a spectrum showing the singly-excited bound-state resonance positions, intensities, and shapes. The product $|p\rangle$ can result from any energy-allowed process, such as spontaneous emission or ionization by a second photon absorption. Such spectra achieve very high resolution (1 MHz, for example, in Refs. [6–8]) because the kinetic energy spread in a trap of ultracold atoms can be of the same order of magnitude as the natural width of the cooling transition [1].

Not too long ago, a Feshbach-resonance formula was used with much success in the context of high-resolution photoassociation spectra of colliding ultracold alkali-metal atoms [14]:

$$P_p(E, l, \Delta_b) = \frac{\gamma_s(E, l)\Gamma_p}{(E - \hbar\Delta_b)^2 + \left(\frac{\gamma_t}{2}\right)^2} , \qquad (1)$$

where $\hbar\Delta_b \equiv E_b - \hbar\omega$, E_b is the position of the resonance measured from the zero energy asymptote of the two-atom-system ground state $|g\rangle$, E is the asymptotic relative kinetic energy of the colliding atoms, $\gamma_s(E, l)/\hbar$ is the stimulated-emission rate back to the ground state, $\Gamma_p/\hbar$ is the rate at which the bound-state resonance decays to the product states $|p\rangle$, and $\gamma_t \equiv \Gamma_p + \gamma_s(E, l)$. The quantity $P_p(E, l, \Delta_b)$ is the opacity function entering the expression of the cross section $\sigma_p(E, \Delta_b)$ for the decay from the excited resonance to product states collectively labeled p,

$$\sigma_p(E, \Delta_b) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l + 1)P_p(E, l, \Delta_b) , \qquad (2)$$

where l is the rotational-angular-momentum quantum number labeling the partial wave in the entrance-channel state $|g\rangle$ and $k > 0$ is the wave number obtained from

$$E = \frac{\hbar^2 k^2}{2\mu} , \qquad (3)$$

where μ is the reduced mass of the two-atom system. The photoassociation spectrum is proportional to the

rate coefficient, $K_p(T, \omega)$, for the inelastic processes forming products $|p\rangle$ from the two colliding ground-state atoms. This rate coefficient is defined in terms of Eq. (2) as

$$K_p(T, \omega) = \langle v_{rel}\sigma_p(E, \omega)\rangle_T \ , \qquad (4)$$

where v_{rel} is the relative speed at which the atoms approach each other from infinity and the brackets $\langle ... \rangle_T$ imply an average over the distribution of relative speeds v_{rel} corresponding to the temperature T. The thermally-averaged line shapes described by Eq. (4) carry information about the partial waves involved in the collisions, the temperature of the atomic sample, and the details of the ground-state potential, such as the value of its scattering length [14].

The scattering lengths of ground-state elastic collisions have received renewed attention now that Bose-Einstein condensation of alkali-metal atoms has been evidenced experimentally [15–17]. For elastic s-wave collisions ($l = 0$) of neutral alkali-metal atoms, we can prove that, in the very low energy limit, the phase shift η_0 goes as $\eta_0 \approx -ka$, where k is the wave number in Eq. (3) and a is defined as the scattering length [18]. Knowing the sign of a is important because a positive scattering length ensures that the condensate will be stable against collapse [19]. However, if $a < 0$ there can be no Bose-Einstein phase transition in a homogeneous gas [20]. In the recent experiments, the ultracold samples have reached temperatures lower than 1 μK and densities between 10^{12} and 10^{14} atoms/cm^3 in magnetic traps that break the homogeneity of the gas [15–17]. For these trapped samples, even when $a < 0$, if the interatomic interaction is much smaller than the external-potential level spacing, a metastable Bose-Einstein condensate is predicted to form [21]. Hence, the knowledge of the scattering-length sign is of crucial importance in connection with the Bose-Einstein condensation of trapped alkali-metal species. As predicted in Ref. [14], experimental photoassociation spectra in conjunction with theoretical analysis assisted by Eq. (1) do allow accurate determination of scattering lengths of alkali-metal ground-state potentials [22].

Some alkali-metal species have negative ground-state scattering lengths [23]. For example, the ground $^3\Sigma_u^+$ potential of the ^{7}Li diatomic molecule has a scattering length of $a \approx -27.3a_0$ ($1a_0 \equiv 1$ Bohr radius) [10].

Recently, however, Fedichev, Kagan, Shlyapnikov, and Walraven [24] have developed the idea of manipulating the scattering length of an alkali-metal species by using nearly-resonant light. These authors derived a Feshbach-resonance formula in the limit of zero temperature and showed that the sign and magnitude of the scattering length can be changed using a high-intensity laser field, detuned very far to the red of the atomic transition to avoid too much trap loss due to photon recoil. Their formulation can be described by considering a situation very similar to photoassociation, the essential difference being that the frequency detuning with respect to the bound state $|b\rangle$ must be much greater than the resonance linewidth, so that the photon absorption is a virtual process. This condition must be satisfied because, in the case of a Bose-Einstein condensate, photoassociation is followed by spontaneous emission and increased loss from the trap, decreasing the condensate lifetime. In Ref. [24], Fedichev, Kagan, Shlyapnikov, and Walraven establish the possibility to change the scattering length substantially without appreciable photoassociation or recoil losses and illustrate their achievement for ^{7}Li.

Inspired by the fact that the experiments on Bose-Einstein condensation were realized at finite ultracold temperatures [15–17], in this paper we generalize the approach of Ref. [24] to the case of finite collision energies. Reference [24] assumed an excited-state lifetime that is independent of the interatomic separation. In our formalism we allow for the excited-state lifetime to be a function of the interatomic distance, as it is the case in a real system [25]. For example, in Ref. [14] the values of Γ_p/h for the 48th and 85th vibrational levels of the excited 1_g sodium-dimer potential are, respectively, 0.0746 and 9.76 MHz, corresponding to the respective temperatures of $\Gamma_p/k_B = 3.58$ and 468 μK. This difference in decay widths is a consequence of the long-range Hund's case (c) 1_g state adiabatically changing into a Hund's case (a) $^1\Pi_g$ state at short range. Decay of this $^1\Pi_g$ state is forbidden by electric-dipole interactions to either the $^1\Sigma_g^+$ or $^3\Sigma_u^+$ ground states, since the transition dipole of the 1_g state rapidly approaches zero as R decreases and the electronic binding energy becomes larger than the $^2P_{3/2}$ - $^2P_{1/2}$ fine-structure splitting. Because the 48th vibrational state is localized within about 6 and $27a_0$ and the 85th vibrational

state within about 6 and $111a_0$, the former is essentially a long-lived Hund's case (a) $^1\Pi_g$ state, while the latter has a strong component of the short-lived Hund's case (c) 1_g state. These very different lifetimes are the reason why the 48th and 85th vibrational-state features show significantly different shapes. The narrow 48th vibrational state exhibits almost no natural broadening, where most of the broadening is purely thermal. In contrast, the large natural width of the 85th vibrational state gives rise to a much broader resonance line shape. The R-dependence of the lifetime is also very relevant in the context of light control of the scattering length, as we will discuss in this paper. We also show that the resonant-scattering formula of Eq. (1), used in Ref. [14], can be derived from our present approach. In the sections that follow we present the details of our full two-channel theory in a very didactic derivation.

II. Description of the model

In this section we present a simple two-channel model capable of predicting the modification of the ground-state scattering length caused by a high-intensity laser field, and also the essential features of line shapes of high-resolution photoassociation spectra of ultracold atoms. We assume that the bound state $|b\rangle$ decays to the product states $|p\rangle$, which are detected. For simplicity, we take spontaneous emission as the only process through which the product states $|p\rangle$ are formed. Of course the modification of the ground-state scattering length we are calculating has to be re-

alized with minimal spontaneous emission, as explained above, because otherwise there would be excessive escape from the trap. In the case of the photoassociation spectrum, the opposite is desired, that is, spontaneous emission has to be maximal. Therefore, the spectrum corresponds to the total spontaneous fluorescence from the molecular excited bound state $|b\rangle$ as a function of the photoexcitation frequency ω.

Simple models of resonant collisions can be found in basic textbooks [18]. However, it is not trivial to find a simple formalism that incorporates spontaneous emission from the molecular excited bound state. A straightforward way of simulating decay from the molecular excited bound state is to introduce an imaginary part in the electronic-potential function of this state. This procedure introduces a term proportional to the probability density in the continuity equation derived from Schrödinger's equation. Such a term will cause the corresponding eigenfunction norm to decrease, implying nonconservation of probability. We can eliminate this apparent deficiency by arguing that the missing probability can be found in the states populated after the decay. To illustrate this argument, let us consider the Schrödinger equation for the case of a single potential $V_1(R)$:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{R},t) + V_1(R)\psi(\vec{R},t) = i\hbar\frac{\partial\psi(\vec{R},t)}{\partial t} \ . \quad (5)$$

If we assume that $V_1(R)$ is a complex function of $R \equiv \left|\vec{R}\right|$, the complex conjugate of Eq. (5) is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi^*(\vec{R},t) + V_1^*(R)\psi^*(\vec{R},t) = -i\hbar\frac{\partial\psi^*(\vec{R},t)}{\partial t} \ . \quad (6)$$

Multiplying Eq. (5) by $\psi^*(\vec{R},t)$ gives

$$-\frac{\hbar^2}{2m}\psi^*(\vec{R},t)\nabla^2\psi(\vec{R},t) + V_1(R)\psi^*(\vec{R},t)\psi(\vec{R},t) = i\hbar\psi^*(\vec{R},t)\frac{\partial\psi(\vec{R},t)}{\partial t} \ , \quad (7)$$

and multiplying Eq. (6) by $\psi(\vec{R},t)$ gives

$$-\frac{\hbar^2}{2m}\psi(\vec{R},t)\nabla^2\psi^*(\vec{R},t) + V_1^*(R)\psi^*(\vec{R},t)\psi(\vec{R},t) = -i\hbar\psi(\vec{R},t)\frac{\partial\psi^*(\vec{R},t)}{\partial t} \ . \quad (8)$$

Subtracting Eq. (8) from Eq. (7) allows us to establish the relation

$$\vec{\nabla}\cdot\vec{J}_\psi(\vec{R},t) + \frac{\partial\rho_\psi(\vec{R},t)}{\partial t} = \frac{V_1(R) - V_1^*(R)}{i\hbar}\rho_\psi(\vec{R},t) \ , \quad (9)$$

where

$$\vec{J}_\psi(\vec{R},t) \equiv \frac{\hbar}{2mi}\left[\psi^*(\vec{R},t)\vec{\nabla}\psi(\vec{R},t) - \psi(\vec{R},t)\vec{\nabla}\psi^*(\vec{R},t)\right] \tag{10}$$

is the probability flux and

$$\rho_\psi(\vec{R},t) \equiv \psi^*(\vec{R},t)\psi(\vec{R},t) \tag{11}$$

is the probability density. Let us define the imaginary part of $V_1(R)$ by

$$-\frac{\gamma_1(R)}{2} \equiv \frac{V_1(R) - V_1^*(R)}{2i} \ . \tag{12}$$

Let us assume that $\gamma_1(R) > 0$. Therefore, integration of Eq. (9) over all space gives

$$\int_{V_\infty} \vec{\nabla} \cdot \vec{J}_\psi(\vec{R},t)d^3R + \frac{d}{dt}\int_{V_\infty} \rho_\psi(\vec{R},t)d^3R = -\frac{1}{\hbar}\int_{V_\infty} \gamma_1(R)\rho_\psi(\vec{R},t)d^3R \ , \tag{13}$$

where V_∞ is the total volume of space and we have used Eq. (12). Assuming that the wavefunctions are zero at infinity and using Gauss' theorem, the first integral in Eq. (13) is zero and we obtain

$$\frac{d}{dt}\int_{V_\infty} \rho_\psi(\vec{R},t)d^3R = -\frac{\Gamma_1(t)}{\hbar} < 0 \ , \tag{14}$$

where we have defined

$$\Gamma_1(t) \equiv \int_{V_\infty} \gamma_1(R)\rho_\psi(\vec{R},t)d^3R \ . \tag{15}$$

Eq. (14) shows that the total probability, $\int_{V_\infty} \rho_\psi(\vec{R},t)d^3R$, is not conserved: it decreases as a function of time. For example, let us suppose that $\gamma_1(R) = \gamma_1$ does not depend on R, as in Ref. [24]. Thus, we can factor $\gamma_1(R)$ out of the integral in Eq. (15) and the total probability, $\int_{V_\infty} \rho_\psi(\vec{R},t)d^3R$, decays with time as

$$\int_{V_\infty} \rho_\psi(\vec{R},t)d^3R = e^{-\gamma_1/\hbar \ t}\int_{V_\infty} \rho_\psi(\vec{R},0)d^3R \ . \tag{16}$$

Reference [26] contains a rigorous derivation of this complex potential approach. Basically, this treatment consists of obtaining an effective potential, also known as an optical potential [18], that is complex. The imaginary part arises because of the probability-flux loss from the excited bound state. Here we will employ this method to treat dissipation, but we could also use others, such as the artificial-channel approach [27].

The model we employ is the following. Asymptotically, the state $|g\rangle$ represents two identical atoms in their ground states. Analogously, $|e\rangle$ is the asymptotic ket for the two atoms with one of them in its first excited state. We assume that $|g\rangle$ and $|e\rangle$ correlate with only two molecular electronic states characterized, respectively, by the nonrelativistic Born-Oppenheimer molecular potentials $V_g(R)$ and $V_e(R)$, where R is the distance between the nuclei of the colliding atoms. For

definiteness, let us suppose that these potentials approach zero as R approaches infinity. Let us further assume, as in the particular case of Ref. [14], that the ground and excited states have opposite parities with respect to inversion about the center of mass of the molecule. Without loss of generality, let $|g\rangle$ and $|e\rangle$ be ungerade and gerade, respectively.

Photons of the laser field are introduced by Fock states $|n\rangle$ containing n laser photons. If $|g,n\rangle$ is the product state describing, asymptotically, the two-atom and laser systems before photon absorption, then $|e, n-1\rangle$ describes these systems after absorption of a photon by one atom. Let $\hbar\omega_0$ be the energy difference between the two-atom states $|g\rangle$ and $|e\rangle$. Thus, if the laser frequency is ω, and, excluding the relative motion, we define the electronic-energy eigenvalue of the state $|g,n\rangle$ to be zero, then the electronic-energy

eigenvalue of $|e, n-1\rangle$ is $\hbar(\omega_0 - \omega)$. These considerations hold asymptotically $(R \to \infty)$ only. For finite R, we have the $|g, n\rangle$ state correlating with, say, $\left|\Psi_1(\vec{R})\right\rangle$, and $|e, n-1\rangle$ with $\left|\Psi_2(\vec{R})\right\rangle$. Therefore, $V_g(R)$ and $V_e(R) + \hbar(\omega_0 - \omega)$ are the electronic energy eigenvalues of $\left|\Psi_1(\vec{R})\right\rangle$ and $\left|\Psi_2(\vec{R})\right\rangle$, respectively. Let us define the R-dependent detuning $\Delta(R)$ as

$$-\hbar\Delta(R) \equiv V_e(R) + \hbar(\omega_0 - \omega) - V_g(R) \ . \qquad (17)$$

As $R \to \infty$, let us denote the asymptotic value of $\Delta(R)$ by Δ and, from Eq. (17),

$$\Delta \equiv \lim_{R\to\infty} \Delta(R) = \hbar(\omega - \omega_0) \ . \qquad (18)$$

From now on, we will consider $\omega_0 > \omega$ (red detuning).

In this model we assume that all quantities are calculated in a reference frame fixed to the internuclear axis of the two-atom system (body-fixed representation). Thus, the excitation by the laser field is represented, in this formalism, by the Rabi coupling $\hbar\Omega(R)$ given by [28]

$$\hbar\Omega(R) = \left(\frac{2\pi}{c} I\right)^{\frac{1}{2}} \mu_M(R) \ , \qquad (19)$$

where I is the laser intensity and $\mu_M(R)$ is the molecular transition electric-dipole moment in the body-fixed representation. We introduce the imaginary part of the excited potential, $-\gamma_p(R)/2$, to simulate spontaneous

emission [26], as discussed above. Notice that $\gamma_p(R)$ is the molecular Einstein A coefficient for spontaneous emission, and, therefore, is proportional to the square of $\mu_M(R)$ [25].

III. The close-coupled equations in the Born-Oppenheimer approximation

To solve the Schrödinger equation for this model, we apply the standard expansion [29]

$$\left|\Phi_\beta(\vec{R})\right\rangle = \sum_{\beta'=1}^{2} \left|\Psi_{\beta'}(\vec{R})\right\rangle \frac{F_{\beta',\beta}(R)}{R} \ , \qquad (20)$$

$\beta = 1, 2$. In Eq. (20) the electronic motion is described by the functions $\left|\Psi_{\beta'}(\vec{R})\right\rangle$, which contain $\vec{R}$ as a parameter vector. The relative motion is described by the $\vec{R}$-dependence of $\left|\Psi_{\beta'}(\vec{R})\right\rangle$ and the R-dependence of the coefficients $F_{\beta',\beta}(R)$. Hence, the time-independent Schrödinger's equation gives the coupled equations:

$$\left\langle \Psi_{\beta''}(\vec{R}) \right| (H - E) \left| \Phi_\beta(\vec{R}) \right\rangle = 0 \ , \qquad (21)$$

where H is the total Hamiltonian for this model and E is the total energy of the system (E is the eigenvalue of H). Notice that E is also equal to the asymptotic relative kinetic energy of the approaching ground-state atoms. Explicitly, from Eqs. (20) and (21), we obtain

$$-\frac{\hbar^2}{2\mu} \sum_{\beta'=1}^{2} \left\langle \Psi_1(\vec{R}) \right| \frac{\partial^2}{\partial R^2} \left[F_{\beta',\beta}(R) \left| \Psi_{\beta'}(\vec{R}) \right\rangle \right] + \sum_{\beta'=1}^{2} \frac{\left\langle \Psi_1(\vec{R}) \left| \vec{l}^{\,2} \right| \Psi_{\beta'}(\vec{R}) \right\rangle}{2\mu R^2} F_{\beta',\beta}(R) + V_g(R) F_{1,\beta}(R)$$

$$+ \hbar\Omega(R) F_{2,\beta}(R) - E F_{1,\beta}(R) = 0 \ , \qquad (22)$$

and

$$-\frac{\hbar^2}{2\mu} \sum_{\beta'=1}^{2} \left\langle \Psi_2(\vec{R}) \right| \frac{\partial^2}{\partial R^2} \left[F_{\beta',\beta}(R) \left| \Psi_{\beta'}(\vec{R}) \right\rangle \right] + \sum_{\beta'=1}^{2} \frac{\left\langle \Psi_2(\vec{R}) \left| \vec{l}^{\,2} \right| \Psi_{\beta'}(\vec{R}) \right\rangle}{2\mu R^2} F_{\beta',\beta}(R) + \hbar\Omega(R) F_{1,\beta}(R)$$

$$+ \left[V_e(R) + \hbar(\omega_0 - \omega) - i\frac{\gamma_p(R)}{2} \right] F_{2,\beta}(R) - E F_{2,\beta}(R) = 0 \ , \qquad (23)$$

where $\beta = 1, 2$, $\vec{l}$ is the relative rotational-angular-momentum operator of the atoms, μ is the reduced atomic mass, and we have introduced the Rabi coupling of Eq. (19). Now let us consider the radial terms of the form

$$\left\langle \Psi_{\beta''}(\vec{R}) \right| \frac{\partial^2}{\partial R^2} \left[F_{\beta',\beta''}(R) \left| \Psi_{\beta'}(\vec{R}) \right\rangle \right] = \frac{\partial^2 F_{\beta',\beta''}(R)}{\partial R^2} \delta_{\beta',\beta''} + 2\frac{\partial F_{\beta',\beta''}(R)}{\partial R} \left\langle \Psi_{\beta''}(\vec{R}) \right| \frac{\partial}{\partial R} \left| \Psi_{\beta'}(\vec{R}) \right\rangle$$

$$+ F_{\beta',\beta''}(R) \left\langle \Psi_{\beta''}(\vec{R}) \right| \frac{\partial^2}{\partial R^2} \left| \Psi_{\beta'}(\vec{R}) \right\rangle \ , \qquad (24)$$

where the inner product $\left\langle \Psi_{\beta''}(\vec{R}) \middle| (\partial^2/\partial R^2) \left[F_{\beta',\beta''}(R) \middle| \Psi_{\beta'}(\vec{R}) \right\rangle \right]$ does not include an integration over $\vec{R}$, since the ket and bra notations refer to the electronic coordinates only, and $\vec{R}$ is just a parameter vector with respect to the electronic motion. Let us call the quantities $\left\langle \Psi_{\beta''}(\vec{R}) \middle| (\partial/\partial R) \middle| \Psi_{\beta'}(\vec{R}) \right\rangle$ and $\left\langle \Psi_{\beta''}(\vec{R}) \middle| (\partial^2/\partial R^2) \middle| \Psi_{\beta'}(\vec{R}) \right\rangle$ "the radial Born-Oppenheimer matrix elements". For $\beta' \neq \beta''$, because $\left| \Psi_1(\vec{R}) \right\rangle$ is ungerade and $\left| \Psi_2(\vec{R}) \right\rangle$ is gerade, we get

$$\left\langle \Psi_{\beta''}(\vec{R}) \middle| \frac{\partial}{\partial R} \middle| \Psi_{\beta'}(\vec{R}) \right\rangle = \left\langle \Psi_{\beta''}(\vec{R}) \middle| \frac{\partial^2}{\partial R^2} \middle| \Psi_{\beta'}(\vec{R}) \right\rangle = 0 \ , \tag{25}$$

since $\partial/\partial R$ and $\partial^2/\partial R^2$ are invariant under inversion of electronic coordinates. We will also neglect the diagonal ($\beta' = \beta''$) radial Born-Oppenheimer matrix elements as compared to $V_g(R)$ and $V_e(R)$ because these terms are negligible in the Born-Oppenheimer approximation, which amounts to recognizing that the electronic motion is much faster than the relative nuclear motion, due to the fact that the nuclei are much more massive than the electrons [28]. Accordingly, we will neglect all derivatives of $\left| \Psi_{\beta'}(\vec{R}) \right\rangle$ with respect to R in our model.

Now let us consider the matrix elements $\left\langle \Psi_{\beta''}(\vec{R}) \middle| \vec{l}^{\,2} \middle| \Psi_{\beta'}(\vec{R}) \right\rangle$. Again, because $\left| \Psi_1(\vec{R}) \right\rangle$ is ungerade and $\left| \Psi_2(\vec{R}) \right\rangle$ is gerade, we obtain

$$\left\langle \Psi_{\beta''}(\vec{R}) \middle| \vec{l}^{\,2} \middle| \Psi_{\beta'}(\vec{R}) \right\rangle = \left\langle \Psi_{\beta'}(\vec{R}) \middle| \vec{l}^{\,2} \middle| \Psi_{\beta'}(\vec{R}) \right\rangle \delta_{\beta',\beta''} = \hbar^2 l_{\beta'}(l_{\beta'}+1)\delta_{\beta',\beta''}$$
$$+ \left\langle \Psi_{\beta'}(\vec{R}) \middle| \left[\vec{l}^{\,2} - \hbar^2 l_{\beta'}(l_{\beta'}+1) \right] \middle| \Psi_{\beta'}(\vec{R}) \right\rangle \delta_{\beta',\beta''} \ , \tag{26}$$

where $\hbar^2 l_{\beta'}(l_{\beta'}+1)$ ($l_{\beta'} = 0,1,2,...$) is the eigenvalue of $\vec{l}^{\,2}$ corresponding to the eigenfunction $Y_{l_{\beta'}}^{m_l}(\theta,\varphi)$:

$$\vec{l}^{\,2} Y_{l_{\beta'}}^{m_l}(\theta,\varphi) = \hbar^2 l_{\beta'}(l_{\beta'}+1) Y_{l_{\beta'}}^{m_l}(\theta,\varphi) \ , \tag{27}$$

where $Y_{l_{\beta'}}^{m_l}(\theta,\varphi)$ is a Spherical Harmonic function, $m_l = -l_{\beta'}, -l_{\beta'}+1, ..., l_{\beta'}$ indicates the quantum number associated with the projection of $\vec{l}$ along the quantization axis, and (θ,φ) are the polar coordinates of $\vec{R}$ with respect to a space-fixed reference frame. We will also neglect the "angular Born-Oppenheimer matrix elements", $\left\langle \Psi_{\beta'}(\vec{R}) \middle| \left[\vec{l}^{\,2} - \hbar^2 l_{\beta'}(l_{\beta'}+1) \right] \middle| \Psi_{\beta'}(\vec{R}) \right\rangle$, as compared to $V_g(R)$ and $V_e(R)$, because these terms also are small in the Born-Oppenheimer approximation [28].

In this model we further assume that the ground state $\left| \Psi_1(\vec{R}) \right\rangle$ is an eigenfunction of $\vec{l}^{\,2}$ with quantum number l, that is, $\vec{l}^{\,2} \left| \Psi_1(\vec{R}) \right\rangle = \hbar^2 l(l+1) \left| \Psi_1(\vec{R}) \right\rangle$, and that $\vec{l}^{\,2} \left| \Psi_2(\vec{R}) \right\rangle = 0$ because the centrifugal term is negligibly small (of the order of $\hbar^2/(2\mu R^2) \approx 0.05 \text{ cm}^{-1}$ ($R \approx 10a_0$) in Ref. [14]) as compared to the excited-state dissociation energy ($\sim 76 \text{ cm}^{-1}$ in Ref. [14]) and the average value of the excited potential between the inner and outer classical turning points of the resonance. From now on, we assume that the asymptotic relative kinetic energy of the entrance channel, E, is less than $\hbar(\omega_0 - \omega)$.

Let us express Eqs. (22) and (23) as the system of equations

$$\frac{d^2 F_{1,\beta}(R)}{dR^2} + \left(k^2 - U_g(R) \right) F_{1,\beta}(R) = \Theta(R) F_{2,\beta}(R) \ , \tag{28}$$

$$\frac{d^2 F_{2,\beta}(R)}{dR^2} - \left(\kappa^2 + U_e(R) - i\xi(R) \right) F_{2,\beta}(R) = \Theta(R) F_{1,\beta}(R) \ , \tag{29}$$

where $k > 0$ is defined in Eq. (3),

$$U_g(R) \equiv \frac{2\mu}{\hbar^2}\left(V_g(R) + \frac{\hbar^2 l(l+1)}{2\mu R^2}\right) , \qquad (30)$$

$$\kappa^2 \equiv -\frac{2\mu}{\hbar^2}\left(E + \hbar\Delta\right) > 0 , \qquad (31)$$

$$U_e(R) \equiv \frac{2\mu}{\hbar^2}V_e(R) , \qquad (32)$$

$$\xi(R) \equiv \frac{\mu}{\hbar^2}\gamma_p(R) , \qquad (33)$$

and

$$\Theta(R) \equiv \frac{2\mu}{\hbar}\Omega(R) . \qquad (34)$$

In Eqs. (28) and (29), $\beta = 1, 2$ indicates whether the colliding atoms are, initially, in state $\left|\Psi_1(\vec{R})\right\rangle$ ($\beta = 1$) or $\left|\Psi_2(\vec{R})\right\rangle$ ($\beta = 2$). Since the collision partners approach each other in the ground state $\left|\Psi_1(\vec{R})\right\rangle$, we will consider the case in which $\beta = 1$. Notice that in Eqs. (28) and (29) we have already taken the Born-Oppenheimer approximation into account by neglecting the radial and angular Born-Oppenheimer matrix elements appearing in Eqs. (24) and (26), as described above.

IV. The closed-channel wavefunction

Because $E < -\hbar\Delta$, we say that $\left|\Psi_2(\vec{R})\right\rangle$ is a closed channel, that is, the probability of finding the system in the state $\left|\Psi_2(\vec{R})\right\rangle$ as $R \to \infty$ is zero. The radial function $F_{2,1}(R)$ can be expanded as a linear superposition of the eigenfunctions of Eq. (29) with $\Theta(R) = 0$ and $\xi(R) = 0$:

$$F_{2,1}(R) = \sum_n a_n \phi_n(R) + \int_0^\infty g(k')\phi(k', R)dk' , \quad (35)$$

where a_n and $g(k')$ are the expansion coefficients, the sum over n accounts for the discrete spectrum of negative eigenvalues $-\kappa_n^2$ and eigenvectors $\phi_n(R)$:

$$\frac{d^2\phi_n(R)}{dR^2} - \left(\kappa_n^2 + U_e(R)\right)\phi_n(R) = 0 , \qquad (36)$$

and the integral over k' accounts for the continuous spectrum of positive eigenvalues $(k')^2$ and eigenvectors $\phi(k', R)$:

$$\frac{d^2\phi(k', R)}{dR^2} + \left((k')^2 - U_e(R)\right)\phi(k', R) = 0 . \qquad (37)$$

From Eqs. (29), (35), (36), and (37), we obtain

$$\sum_n a_n \left[\frac{d^2}{dR^2} - \left(\kappa^2 + U_e(R)\right)\right]\phi_n(R) + \int_0^\infty g(k')\left[\frac{d^2}{dR^2} - \left(\kappa^2 + U_e(R)\right)\right]\phi(k', R)dk'$$

$$= \sum_n a_n \left(\kappa_n^2 - \kappa^2\right)\phi_n(R) - \int_0^\infty g(k')\left((k')^2 + \kappa^2\right)\phi(k', R)dk' = \Theta(R)F_{1,1}(R) - i\xi(R)F_{2,1}(R) . \qquad (38)$$

Therefore, using the normalization relations for $\phi_n(R)$ and $\phi(k', R)$,

$$\int_0^\infty \phi_{n'}^*(R)\phi_n(R)dR = \delta_{n',n} \qquad (39)$$

and

$$\int_0^\infty \phi^*(k'', R)\phi(k', R)dR = \delta(k'' - k') , \qquad (40)$$

from Eq. (38), we find

$$a_n = \frac{\langle n|\Theta|1\rangle - i\langle n|\xi|2\rangle}{\kappa_n^2 - \kappa^2} , \qquad (41)$$

and

$$g(k') = -\frac{\langle k'|\Theta|1\rangle - i\langle k'|\xi|2\rangle}{(k')^2 + \kappa^2} , \qquad (42)$$

where we have defined

$$\langle n| \Theta |1\rangle \equiv \int_0^\infty \phi_n^*(R)\Theta(R)F_{1,1}(R)dR \ , \tag{43}$$

$$\langle n| \xi |2\rangle \equiv \int_0^\infty \phi_n^*(R)\xi(R)F_{2,1}(R)dR \ , \tag{44}$$

$$\langle k'| \Theta |1\rangle \equiv \int_0^\infty \phi^*(k',R)\Theta(R)F_{1,1}(R)dR \ , \tag{45}$$

and

$$\langle k'| \xi |2\rangle \equiv \int_0^\infty \phi^*(k',R)\xi(R)F_{2,1}(R)dR \ . \tag{46}$$

Hence, Eqs. (35), (41), and (42) give

$$F_{2,1}(R) = \sum_n \frac{\langle n| \Theta |1\rangle - i\langle n| \xi |2\rangle}{\kappa_n^2 - \kappa^2}\phi_n(R) - \int_0^\infty \frac{\langle k'| \Theta |1\rangle - i\langle k'| \xi |2\rangle}{(k')^2 + \kappa^2}\phi(k',R)dk' \ . \tag{47}$$

Now let us suppose $-\kappa^2$ is very close to the eigenvalue $-\kappa_b^2$ of the eigenfunction $\phi_b(R)$. Let us also assume that the particular eigenvalue $-\kappa_b^2$ is sufficiently distant from any other eigenvalue $-\kappa_{n\neq b}^2$, such that the greatest contribution to Eq. (47) comes from the term for which $n = b$ ($\phi_b(R)$ is said to be an "isolated resonance"). Later we will clearly see that the absolute value of the difference between $-\kappa_b^2$ and the corresponding eigenvalues $-\kappa_{n\neq b}^2$ of the first-neighbor resonances of $\phi_b(R)$ must be much greater than the width of resonance $\phi_b(R)$ in order for $\phi_b(R)$ to be an isolated resonance. Neglecting all the non-resonant terms in the expansion of Eq. (47) gives

$$F_{2,1}(R) = \frac{\langle b| \Theta |1\rangle - i\langle b| \xi |2\rangle}{\kappa_b^2 - \kappa^2}\phi_b(R) \ . \tag{48}$$

This approximation is equivalent to neglecting the non-local effects introduced by the non-resonant terms [18]. Multiplying Eq. (48) by $\phi_b^*(R)\xi(R)$, integrating over R, and solving for $\langle b| \xi |2\rangle$ gives

$$\langle b| \xi |2\rangle = \frac{\langle b| \xi |b\rangle \langle b| \Theta |1\rangle}{\kappa_b^2 - \kappa^2 + i\langle b| \xi |b\rangle} \ , \tag{49}$$

where we have defined

$$\langle b| \xi |b\rangle \equiv \int_0^\infty \phi_b^*(R)\xi(R)\phi_b(R)dR \ . \tag{50}$$

Therefore, Eqs. (48) and (49) imply

$$F_{2,1}(R) = \frac{\langle b| \Theta |1\rangle}{\kappa_b^2 - \kappa^2 + i\langle b| \xi |b\rangle}\phi_b(R) \ . \tag{51}$$

It is apparent from Eq. (51) that $F_{2,1}(R)$ has a finite extension, since $\phi_b(R)$ is a bound state.

V. The open-channel wavefunction and the S-matrix

So far we have not made any assumptions regarding the asymptotic behavior of the imaginary part of the excited-state potential, here represented by $-\xi(R)$. Because, in actual numerical calculations, the bound states $\phi_b(R)$ that we investigate do not extend to infinity (in Ref. [14], for example, $\phi_b(R)$ did not extend over about $120a_0$), the assumed behavior of $-\xi(R)$ as $R \to \infty$ is immaterial. Hence, we will assume, from now on, that $-\xi(R)$ goes to zero asymptotically and assumes its realistic behavior within the extension of the bound state $\phi_b(R)$. As a consequence, since $\Theta(R)$ is proportional to the molecular transition electric-dipole moment $\mu_M(R)$ and $-\xi(R)$ is proportional to the square of $\mu_M(R)$, $\Theta(R)$ also goes to zero as $R \to \infty$. These assumptions allow us to employ the asymptotic analysis of standard scattering theory [28] as follows. The wavefunction $F_{1,1}(R)$, satisfying Eq. (28), in contrast to $F_{2,1}(R)$ (see Eq. (51)), can extend to infinity, and,

therefore, is called an open-channel wavefunction. In this problem we have only one open channel, namely, $\left|\Psi_1(\vec{R})\right\rangle$. The S-matrix for this problem, which has only one element, is given in terms of the asymptotic form of the solution $F_{1,1}(R)$ of Eq. (28):

$$F_{1,1}(R \to \infty) \to A_l(k) \left(e^{-i(kR - l\pi/2)} - S_{1,1} e^{i(kR - l\pi/2)} \right) \ , \tag{52}$$

where $A_l(k)$ is a factor that depends on k, and $S_{1,1}$ is defined as the S-matrix element for the only open channel in the problem. Thus, $S_{1,1}$ coincides with the S-matrix itself. For the interested reader, further details about scattering theory are found in Ref. [28].

Now let us assume we have obtained a solution $F_0(R)$ of Eq. (28) for $\Theta(R) = 0$:

$$\frac{d^2 F_0(R)}{dR^2} + \left(k^2 - U_g(R) \right) F_0(R) = 0 \ . \tag{53}$$

As is well known from the elementary theory of potential scattering [18], we can choose the asymptotic form of $F_0(R)$ to be

$$F_0(R \to \infty) \to \sin\left(kR + \eta_l - l\frac{\pi}{2} \right) \ , \tag{54}$$

where $\eta_l = \eta_l(k)$ is the elastic phase shift. Moreover, let this be the solution for which $F_0(R = 0) = 0$ [18]. We further assume that we have chosen $F_0(R)$ as a real function of R, since this choice is always allowed, given the reality of Eq. (53) [18]. Let us now consider another solution of Eq. (53) that assumes the following asymptotic behavior:

$$F_c(R \to \infty) \to \frac{1}{k} e^{i(kR + \eta_l - l\pi/2)} \ . \tag{55}$$

Because

$$e^{i(kR + \eta_l - l\pi/2)} = \cos(kR + \eta_l - l\pi/2) + i\sin(kR + \eta_l - l\pi/2) \ , \tag{56}$$

we can express the solution $F_c(R)$ as

$$F_c(R) = \frac{1}{k} F_r(R) + \frac{i}{k} F_0(R) \ , \tag{57}$$

where $F_r(R)$ is a real function of R and

$$F_r(R \to \infty) \to \cos(kR + \eta_l - l\pi/2) \ . \tag{58}$$

A particular solution of Eq. (28) that vanishes at $R = 0$ is given by

$$F_e(R) = F_0(R) \int_\infty^R dR' F_c(R') \Theta(R') F_{2,1}(R') - F_c(R) \int_0^R F_0(R') \Theta(R') F_{2,1}(R') dR' \ , \tag{59}$$

which can be verified by substituting it into Eq. (28) and using the fact that $F_0(R)$ and $F_c(R)$ satisfy Eq. (53). As $R \to \infty$, we obtain

$$F_e(R \to \infty) \to -\frac{1}{k} e^{i(kR + \eta_l - l\pi/2)} \int_0^\infty F_0(R') \Theta(R') F_{2,1}(R') dR' \tag{60}$$

from Eqs. (54) and (55). Let us define the Green function $G(R, R')$ by

$$G(R, R') \equiv -F_0(R)F_c(R')\theta(R' - R) - F_c(R)F_0(R')\theta(R - R') , \tag{61}$$

where $\theta(R' - R)$ is the step function defined as

$$\theta(R' - R) = \left\{ \begin{array}{l} 1 \ , \text{if} R' \geq R \\ 0 \ , \text{if} R' < R \end{array} \right\} . \tag{62}$$

Thus, Eq. (59) can be written as

$$F_e(R) = \int_0^\infty G(R, R')\Theta(R')F_{2,1}(R')dR' . \tag{63}$$

The function $F_e(R)$ is not the general solution of Eq. (28), because it gives zero if $\Theta(R) = 0$ and it does not have the asymptotic form of Eq. (52) (see Eq. (60)). To build the complete solution, we need the linear combination

$$F_{1,1}(R) = B_l(k)F_0(R) + C_l(k)F_e(R) , \tag{64}$$

where $B_l(k)$ and $C_l(k)$ are coefficients to be determined. Substituting Eq. (64) into Eq. (28) gives

$$C_l(k) = 1 . \tag{65}$$

By imposing the asymptotic form of Eq. (52) to Eq. (64), we obtain

$$B_l(k) = -2iA_l(k)e^{i\eta_l} , \tag{66}$$

and

$$\int_0^\infty F_0(R')\Theta(R')F_{2,1}(R')dR' = kA_l(k)\left(S_{1,1}e^{-i\eta_l} - e^{i\eta_l}\right) , \tag{67}$$

where we have used the asymptotic behaviors of Eqs. (54) and (60). Multiplying Eq. (64) by $\phi_b^*(R)\Theta(R)$, integrating over R, and using the definition in Eq. (43) gives

$$\langle b| \Theta |1 \rangle = B_l(k) \langle b| \Theta |0 \rangle + \langle b| \Theta |e \rangle , \tag{68}$$

where we have used Eq. (65) and defined

$$\langle b| \Theta |0 \rangle \equiv \int_0^\infty \phi_b^*(R)\Theta(R)F_0(R)dR \tag{69}$$

and

$$\langle b| \Theta |e \rangle \equiv \int_0^\infty \phi_b^*(R)\Theta(R)F_e(R)dR = \int_0^\infty \int_0^\infty \phi_b^*(R)\Theta(R)G(R, R')\Theta(R')F_{2,1}(R')dRdR'$$
$$= \frac{\langle b| \Theta |1 \rangle \, \Xi_{b,b}}{\kappa_b^2 - \kappa^2 + i \langle b| \xi |b \rangle} , \tag{70}$$

where we have used Eqs. (51) and (63), and we have defined

$$\Xi_{b,b} \equiv \int_0^\infty \int_0^\infty \phi_b^*(R)\Theta(R)G(R, R')\Theta(R')\phi_b(R')dRdR' . \tag{71}$$

From Eqs. (68) and (70) we obtain

$$\langle b| \Theta |1 \rangle = \frac{B_l(k) \langle b| \Theta |0 \rangle \left(\kappa_b^2 - \kappa^2 + i \langle b| \xi |b \rangle\right)}{\left(\kappa_b^2 - \kappa^2 + i \langle b| \xi |b \rangle - \Xi_{b,b}\right)} . \tag{72}$$

Eqs. (51) and (67) give

$$\langle b | \Theta | 1 \rangle = \frac{k A_l(k) \left(S_{1,1} e^{-i\eta_l} - e^{i\eta_l} \right) \left(\kappa_b^2 - \kappa^2 + i \langle b | \xi | b \rangle \right)}{\int_0^\infty F_0(R') \Theta(R') \phi_b(R') dR'} \; . \tag{73}$$

From Eqs. (66), (72), and (73) it follows that

$$S_{1,1} e^{-2i\eta_l} = \left(1 - \frac{2i \, |\langle b | \Theta | 0 \rangle|^2}{k \left(\kappa_b^2 - \kappa^2 + i \langle b | \xi | b \rangle - \Xi_{b,b} \right)} \right) \; , \tag{74}$$

where, from Eq. (69),

$$\langle 0 | \Theta | b \rangle \equiv \langle b | \Theta | 0 \rangle^* = \int_0^\infty F_0(R') \Theta(R') \phi_b(R') dR' \; , \tag{75}$$

for we have chosen $F_0(R)$ as a real function. So far we have not restricted $\phi_b(R)$ to be real, but, given the form of Eq. (36), we are allowed to suppose that $\phi_b(R)$ is a real function of R to simplify our calculations. Let us denote the real and imaginary parts of $\Xi_{b,b}$ by $Re(\Xi_{b,b})$ and $Im(\Xi_{b,b})$, respectively:

$$\Xi_{b,b} = Re(\Xi_{b,b}) + i Im(\Xi_{b,b}) \; . \tag{76}$$

Employing Eq. (57), Eq. (61) becomes

$$G(R, R') = -\frac{1}{k} F_0(R) F_r(R') \theta(R' - R) - \frac{1}{k} F_r(R) F_0(R') \theta(R - R') - \frac{i}{k} F_0(R) F_0(R') \; . \tag{77}$$

From Eqs. (34), (71), (77), and (103) (see the Appendix) we get

$$Im(\Xi_{b,b}) = -\frac{2\mu}{\hbar^2} \pi \, |\langle b | \hbar\Omega | E, l \rangle|^2 \tag{78}$$

and

$$\begin{aligned}
Re(\Xi_{b,b}) &= -\frac{1}{k} \int_0^\infty \Theta(R') \phi_b(R') F_r(R') dR' \int_0^{R'} \phi_b^*(R) \Theta(R) F_0(R) dR \\
&\quad - \frac{1}{k} \int_0^\infty \phi_b^*(R) \Theta(R) F_r(R) dR \int_0^R \phi_b(R') \Theta(R') F_0(R') dR' \\
&= -\frac{2}{k} \int_0^\infty \Theta(R') \phi_b(R') F_r(R') dR' \int_0^{R'} \phi_b(R) \Theta(R) F_0(R) dR \; ,
\end{aligned} \tag{79}$$

where we have used Eq. (34) and the fact that $\phi_b(R)$ is a real function of R. As it will become evident in the next sections, Eq. (79) essentially gives a shift in the position of the bound-state resonance, while Eq. (78) gives the resonance power broadening.

VI. Modification of the scattering length by light

Equation (103) of the Appendix defines the normalized continuum radial function $F_{E,l}(R)$, which now we use to define the quantity

$$\gamma_s(E, l) \equiv 2\pi \, |\langle b | \hbar\Omega | E, l \rangle|^2 = 2\pi \left[\int_0^\infty \phi_b(R) \hbar\Omega(R) F_{E,l}(R) dR \right]^2 \; . \tag{80}$$

It is evident that $\gamma_s(E, l)/\hbar$ can be viewed as the rate of transition from the bound state $|b\rangle$ back to the energy-normalized ground state $|E, l\rangle$, if we interpret it on the grounds of perturbation theory. From Eqs. (34), (80) and (103) it follows that

$$\gamma_s(E, l) = 2\pi \left[\frac{\hbar^2}{2\mu} \right]^2 |\langle b | \Theta | E, l \rangle|^2 = \frac{\hbar^2}{\mu k} |\langle b | \Theta | 0 \rangle|^2 \; . \tag{81}$$

Let us also define the expectation value

$$\Gamma_p \equiv \langle b | \gamma_p | b \rangle = \int_0^\infty \phi_b(R) \gamma_p(R) \phi_b(R) dR \ , \tag{82}$$

which, from Eq. (33), can also be written as

$$\Gamma_p \equiv \frac{\hbar^2}{\mu} \langle b | \xi | b \rangle \ . \tag{83}$$

Here it is interesting to notice that $\Gamma_p/\hbar$, as written in Eq. (82), is the average spontaneous decay rate from the bound state $|b\rangle$.

Using Eqs. (31), (76), (81), and (83), we can rewrite Eq. (74) in the form

$$S_{1,1} = S_{1,1}(E, l, \Delta_b) = e^{2i\eta_l} \left(1 - \frac{2i\gamma_s(E, l)}{2(E - \hbar\Delta_b) + i\gamma_t} \right) \ , \tag{84}$$

where we have further defined

$$\hbar\Delta_b \equiv -\frac{\hbar^2}{2\mu}\kappa_b^2 - \hbar\Delta + \frac{\hbar^2}{2\mu} Re(\Xi_{b,b}) \ , \tag{85}$$

and, from Eqs. (78) and (80),

$$\gamma_t \equiv \Gamma_p - \frac{\hbar^2}{\mu} Im(\Xi_{b,b}) = \Gamma_p + \gamma_s(E, l) \ . \tag{86}$$

Notice that $\gamma_t/\hbar$ is nothing but the total rate at which the state $|b\rangle$ decays through spontaneous and stimulated emission.

Equation (84) is central to our exposition. It is from this equation that we can derive the modification of the scattering length due to the light field and also the shape of photoassociation spectral lines in a unified fashion. The line shapes will be discussed in the next section. Here we focus on the modification of the scattering length. As explained in Sec. V, $\eta_l = \eta_l(k)$ is the unmodified elastic phase shift. From Eqs. (54) and (103) we obtain the asymptotic form of the unmodified ground-state s-wave radial function:

$$F_{E,0}(R \to \infty) \to \sqrt{\frac{2\mu}{\pi k \hbar^2}} \sin(kR + \eta_0(k)) \ . \tag{87}$$

As mentioned in the Introduction, if k is small enough, then $\eta_0(k) \approx -ka$ for neutral alkali-metal atoms, where a is a quantity that does not depend on k and is defined as the scattering length [18]. In this case, Eq. (87) gives

$$F_{E,0}(R \to \infty) \to \sqrt{\frac{2\mu k}{\pi \hbar^2}} (R - a) \ , \tag{88}$$

from which we can appreciate the meaning of a as the value at which the asymptotic form of $F_{E,0}(R)$ crosses the R axis.

Notice that if there is no light present, then $\gamma_s(E, l) = 0$ and Eq. (84) implies $S_{1,1} = e^{2i\eta_l}$, as it should. If there is light present, we define the complex quantity $\Lambda_l = \Lambda_l(k)$ by writing

$$S_{1,1} \equiv e^{2i\Lambda_l} \tag{89}$$

and, in the limit of small enough k, for s-wave ($l = 0$) scattering, Eq. (84) implies

$$\begin{aligned} e^{2i\Lambda_0} &= e^{-2ika} \left(1 - \frac{2i\gamma_s(E, 0)}{2(E - \hbar\Delta_b) + i\gamma_t} \right) \\ &\approx (1 - 2ika) \left(1 - \frac{2i\gamma_s(E, 0)}{2(E - \hbar\Delta_b) + i\gamma_t} \right) \\ &\approx 1 - 2ika - \frac{2i\gamma_s(E, 0)}{2(E - \hbar\Delta_b) + i\gamma_t} \ . \end{aligned} \tag{90}$$

From Eqs. (80) and (88), we see that $\gamma_s(E, 0)$ is also proportional to k in the low-energy limit and, therefore, we can write $\Lambda_0 \approx -kA$ with

$$A = a + \frac{\gamma_s(E, 0)}{k[2(E - \hbar\Delta_b) + i\gamma_t]} \ . \tag{91}$$

Again we see that $A = a$ if there is no light present and Eq. (91) states the modification on the scattering length if photons are present. We can also write Eq. (91) as

$$A = Re(A) + iIm(A) \ , \qquad (92)$$

where

$$Re(A) = a + \frac{2\gamma_s(E,0)(E - \hbar\Delta_b)}{k[4(E - \hbar\Delta_b)^2 + \gamma_t^2]} \ , \qquad (93)$$

and

$$Im(A) = -\frac{\gamma_s(E,0)\gamma_t}{k[4(E - \hbar\Delta_b)^2 + \gamma_t^2]} \ . \qquad (94)$$

It is easily shown that Eqs. (91), (92), (93), and (94) reduce to the results of Ref. [24] in the limit of $k \to 0$, if we let $\gamma_p(R)$ be independent of R. These equations show how the scattering length is modified by light; the modifications being the appearance of an imaginary part and a change in the magnitude, and even in sign, of the real part. The real part of A is important because it enters the mean-field theories describing the Bose-Einstein condensate [24].

VII. Shapes of photoassociation spectral lines

Thorsheim, Weiner, and Julienne [1] obtained a thermally averaged spectrum for Na atoms at 10 mK by using a Breit-Wigner resonant-scattering treatment and assuming $\Gamma_p < k_B T$, where k_B is Boltzmann's constant, T is the temperature of the atomic sample, and Γ_p is the natural width of the resonance $|b\rangle$ in energy units. Because, as we have mentioned in the Introduction, the temperatures in actual trap experiments are of the order of the Doppler temperature T_D, which is about $\Gamma_p/(2k_B) < 1$ mK, the present model has been designed to be valid also for $k_B T < \Gamma_p$ [14].

It is worth noticing that this model does not conserve total probability because the potential matrix of Eqs. (28) and (29) is not Hermitian. The imaginary part of the excited state potential implies that our calculations will yield a nonunitary S-matrix, in contrast to outputs of theories employing conservative Hamiltonians. Therefore, we can interpret the loss of unitarity, $P_p(E, l, \Delta_b)$, in the ground-state channel as:

$$P_p(E, l, \Delta_b) = 1 - |S_{1,1}(E, l, \Delta_b)|^2 \ , \qquad (95)$$

where $S_{1,1}(E, l, \Delta_b)$ is the elastic nonunitary S-matrix of Eq. (84). It is straightforward to prove that Eqs. (84) and (95) give Eq. (1) as the result for $P_p(E, l, \Delta_b)$. Briefly, Eq. (1) is a result of the coupling between the bound molecule (a discrete state) and the continuum part of its ground potential. This coupling means that there is a finite probability for the atoms to become bound, forming a molecule, and then to return to the continuum by spontaneous emission of a photon after an average lifetime equal to $\hbar/\Gamma_p$.

The Wigner threshold law states that, for very low energy E, the quantity $\gamma_s(E, l)$ depends on E as $E^{(2l+1)/2}$ [18]. This energy-dependent onset, according to Eq. (1), gives us information about the partial waves composing the spectral lines [14]. Also, Γ_p is usually less than the atomic transition natural width and renders Eq. (1) a very narrow width, turning this procedure into a very good probing of the velocity distribution in the trap [14]. Moreover, because the continuum wavefunction $F_{E,l}(R)$ is very sensitive to the ground-state potential, we can also draw conclusions about the details of that potential. Since the temperatures of optically cooled and trapped atoms are typically lower than 1 mK, and the Wigner-law behavior is expected to occur for relative kinetic energies corresponding to temperatures lower than 120, 19, 5.3, 1.5, and 0.6 mK, respectively, for Li, Na, K, Rb, and Cs [29], then we can approximate $\gamma_s(E, l) \approx B_l E^{\frac{(2l+1)}{2}}$. As E increases, this approximation is no longer valid, and both the magnitude of B_l and the difference $\left[\gamma_s(E, l) - B_l E^{\frac{(2l+1)}{2}}\right]$ are extremely sensitive to the details of the ground-state potential, as shown in Ref. [14].

VIII. The future of controlling scattering lengths by nearly-resonant light fields and shapes of high-resolution photoassociation spectral lines

In this work we developed the state-of-the-art two-state collision theory of alkali-metal atoms in the regime of finite ultracold temperature. This approach is limited in many respects due to the fact that a two-state model is far from describing a realistic situation. In the regime of temperatures lower than a few hundreds of μK, the alkali-metal-atom hyperfine structure becomes resolvable and we can no longer ignore it [30]. Also, even at moderate intensities of the light field, partial waves higher than the s-wave begin to contribute to the scattering cross sections, and this amounts to including more and more rotational states into the description as the field gets stronger and stronger [28]. All these real-world characteristics indicate the only direction this research will take in the near future: we need to construct multichannel theories to take us beyond the limited two-channel approaches. We are making a

first attempt in that direction by using the formalism of Ref. [28], in which a multichannel model of a binary collision between spinless atoms is treated in a complete fashion, that is, exactly taking into account all the three-dimensional issues involved in the problem. Such an approach has given a successful qualitative description of optical suppression of ultracold collisions in the case of blue detuning. The logical step now is to apply the same theoretical machinery to the red detuning case, investigating how multichannel effects change the simple description depicted here.

IX. Appendix. The normalization of the continuum wavefunction

The function $F_0(R)$ has been normalized such that the asymptotic form of Eq. (54) holds as $R \to \infty$. Now, for a different eigenvalue of Eq. (53), $\tilde{k}^2$, let us denote the corresponding eigenfunction by $\tilde{F}_0(R)$. We seek a normalization factor $N(k)$ such that

$$\int_0^\infty \left[N(\tilde{k})\tilde{F}_0(R') \right] \left[N(k)F_0(R') \right] dR' = \frac{2\mu}{\hbar^2} \delta\left(\tilde{k}^2 - k^2 \right) \ , \tag{96}$$

as is standard in the theory of atomic collisions [31]. Using Eq. (53) and the fact that $\tilde{F}_0(R=0) = F_0(R=0) = 0$, we can derive the following result:

$$\left(\tilde{k}^2 - k^2 \right) \int_0^\infty \tilde{F}_0(R')F_0(R')dR' = \lim_{R \to \infty} \left[\tilde{F}_0(R)\frac{dF_0(R)}{dR} - F_0(R)\frac{d\tilde{F}_0(R)}{dR} \right] \ . \tag{97}$$

From Eq. (54):

$$
\begin{aligned}
\left(\tilde{k}^2 - k^2 \right) \int_0^\infty \tilde{F}_0(R')F_0(R')dR' &= \lim_{R \to \infty} \left[\sin\left(\tilde{k}R + \tilde{\eta}_l - l\frac{\pi}{2} \right) \frac{d\sin\left(kR + \eta_l - l\frac{\pi}{2} \right)}{dR} \right] \\
&\quad - \lim_{R \to \infty} \left[\sin\left(kR + \eta_l - l\frac{\pi}{2} \right) \frac{d\sin\left(\tilde{k}R + \tilde{\eta}_l - l\frac{\pi}{2} \right)}{dR} \right] \\
&= \lim_{R \to \infty} \left[k\sin\left(\tilde{k}R + \tilde{\eta}_l - l\frac{\pi}{2} \right) \cos\left(kR + \eta_l - l\frac{\pi}{2} \right) \right] \\
&\quad - \lim_{R \to \infty} \left[\tilde{k}\sin\left(kR + \eta_l - l\frac{\pi}{2} \right) \cos\left(\tilde{k}R + \tilde{\eta}_l - l\frac{\pi}{2} \right) \right] \ ,
\end{aligned}
\tag{98}
$$

where $\tilde{\eta}_l \equiv \eta_l(\tilde{k})$. Using the relation [32]

$$\lim_{R\to\infty} \frac{1}{\pi} \frac{\sin(Rx)}{x} = \delta(x) \tag{99}$$

and some usual trigonometric relations in Eq. (98), gives

$$\int_0^\infty \tilde{F}_0(R')F_0(R')dR' = \frac{\pi}{2}\delta\left(\tilde{k}-k\right) \;, \tag{100}$$

where we have set $\delta\left(\tilde{k}+k\right) = 0$ because both $\tilde{k}$ and k are assumed to be positive real quantities. Using the identity

$$\delta\left(\tilde{k}-k\right) \equiv 2k\delta\left(\tilde{k}^2-k^2\right) \;, \tag{101}$$

Eqs. (96) and (100) imply:

$$[N(k)]^2 = \frac{2\mu}{\pi k \hbar^2} \;. \tag{102}$$

Therefore, let us define the normalized solution of Eq. (53) as

$$F_{E,l}(R) \equiv \sqrt{\frac{2\mu}{\pi k \hbar^2}} F_0(R) \;. \tag{103}$$

Finally, let us define the very convenient matrix element,

$$\langle b| \Theta |E,l\rangle \equiv \sqrt{\frac{2\mu}{\pi k \hbar^2}} \langle b| \Theta |0\rangle \;, \tag{104}$$

which is used in Sec. VI.

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