

Stationary phase approximation for the strength of optical Feshbach resonances

R. Ciuryło

Institut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziądzka 5/7, 87–100 Toruń, Poland

E. Tiesinga and P. S. Julienne

Atomic Physics Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8423, Gaithersburg, Maryland 20899-8423, USA

(Received 14 November 2005; published 7 August 2006)

Analytic expressions for the width and shift of a photoassociative resonance or an optically induced Feshbach resonance in ultracold collisions are derived using the quasi-classical stationary phase approximation. This approach for the width is applicable over a wider range of cases than the reflection approximation. Possible applications for optical Feshbach resonances between ultracold alkaline-earth-metal atoms, such as Ca and Sr, are discussed. Our approach also applies to photoassociation in gases of heteronuclear alkali-metal atoms.

DOI: [10.1103/PhysRevA.74.022710](https://doi.org/10.1103/PhysRevA.74.022710)

PACS number(s): 34.50.Rk, 34.10.+x, 32.80.Pj

I. INTRODUCTION

The properties of an atomic collision can be modified when the scattering state is coupled to a bound state [1,2]. Such a coupling leads to resonant scattering. One example of resonant scattering is photoassociation in a thermal gas or Bose condensate of ultracold atoms. In this case, an optical Feshbach resonance is induced when two ultracold atoms collide in the presence of laser radiation of a fixed frequency and are coupled by the light to an excited bound state of the corresponding dimer molecule. This coupling, which changes the amplitude and the phase of the scattering wave function, can be controlled by varying the intensity and frequency of the laser radiation.

In photoassociation of trapped ultracold gases, the change of the amplitude of the scattering wave function can be observed as a loss of atoms from the trap. Measurement of this trap loss as a function of the excitation frequency is known as photoassociative spectroscopy (PAS). In PAS, the excited molecular bound state spontaneously decays to a product state, which in many cases is lost from the trap. This kind of spectroscopy has been an important tool in investigating properties of ultracold gases [3–7].

An important parameter characterizing ultracold collisions is the scattering length. It determines, for example, the stability of a Bose condensate. A resonant change of the scattering wave function directly affects the scattering length. Fedichev *et al.* [8] developed the idea of manipulating the scattering length by optically induced Feshbach resonances. This idea has been elaborated on [9,10] and implemented experimentally [11–13].

Optical Feshbach resonances have mainly been investigated for ultracold alkali-metal gases with a strongly allowed electronic transition. If the alkali-metal atoms in the collision are of the same species, the long-range interaction of the excited electronic molecular state formed from one ground and one excited state atom is the resonant dipole interaction, which varies as $1/R^3$ at large interatomic separations R . The van der Waals interaction between two scattering ground state atoms has a much shorter range, varying as $1/R^6$. This difference in the long-range potential, and consequently, the

large difference in the character of the ground and excited state wave function can be exploited in developing quasi-classical approximations for the optical Feshbach resonances. In particular, the analytic reflection approximation (RA) for the light-induced width and shift of the resonances has been successfully used [10,14,15]. If the alkali-metal atoms in the collision are of different species, however, their long-range interaction in the excited state is $1/R^6$ rather than $1/R^3$ and the reflection approximation cannot be expected to be valid.

Another group of systems which are receiving growing experimental [16,17] and theoretical [18,19] interest are ultra-cold alkaline-earth-metal atoms. These species, as well as others with similar electronic structure and very narrow intercombination lines, offer opportunities for new experiments [20–24] that are very different from those that are possible with alkali-metal atoms. Very recently photoassociation near narrow intercombination lines has been measured in Sr [25] and Yb [26]. The interest in atoms such as Ca or Sr is driven, in part, by prospects for new optical-frequency clocks [27,28]. Furthermore, optical Feshbach resonances near an intercombination line hold the promise for practical optical control of ground state scattering properties in ultracold atomic gases [29]. This is especially significant for alkaline earth metal atoms, which do not have magnetically tunable ground state Feshbach resonances like alkali-metal atoms. Because of the very weak resonant dipole contribution to the excited state potential, the quasi-classical description based on the reflection approximation is not valid for intercombination line transitions. Consequently, it is necessary to seek improved approximations for estimating optical Feshbach resonance properties.

The main goal of this work is to determine if suitable analytical expressions for the width and shift of an optical Feshbach resonance can be developed that are not restricted to the reflection approximation. To do this we start from a phase-amplitude representation of the wave function and introduce the stationary phase approximation to obtain more general approximate quasi-classical formulas than given by the reflection approximation. The applicability of these expressions is discussed and illustrated by comparison to the

exact results of quantum mechanical calculations on model systems simulating ultracold collisions of strontium or calcium. We show that the formula for the width provides an adequate improved approximation when the reflection approximation fails, whereas the formula for the shift is generally not adequate. Consequently, accurate shifts need to be calculated numerically using a complete theoretical expression.

II. OPTICALLY INDUCED FESHBACH RESONANCE

Optical Feshbach resonances and the closely related photoassociation process are well described theoretically [8–10]. In this paper, we explore the analytical expressions obtained in Ref. [10] but use the notation of Ref. [19].

Let us focus on the scattering properties of two colliding ground state atoms, labeled g , in the presence of laser radiation. The laser frequency is tuned close to resonance, allowing the formation of the excited molecular bound state labeled e , which can spontaneously decay to a product state labeled p . The decay of the excited bound state e is described by the width Γ_{pe} . The coupling between the ground scattering state g and the excited bound state e due to the presence of light is described by the stimulated width $\Gamma_{eg}(\varepsilon_r, I)$, which depends on the relative kinetic energy ε_r and the light intensity I . The scattering matrix can be expressed analytically [10], and the matrix element describing elastic scattering in the ground state g is

$$S_{gg} = e^{2i\eta_g} \frac{\Delta + \varepsilon_r - E_{eg} - \Delta_e - \frac{i(\Gamma_{eg} - \Gamma_{pe})}{2}}{\Delta + \varepsilon_r - E_{eg} - \Delta_e + \frac{i(\Gamma_{eg} + \Gamma_{pe})}{2}}, \quad (1)$$

where $\Delta = \hbar\omega - E_A$, $\Delta_e = E_e - E_A$, E_e is the energy of an isolated excited molecular bound level, E_A is energy of one ground state and one excited state atom, ω is the frequency of the light driving the transition, and η_g is the elastic-scattering phase shift in state g in the absence of light. The shift in the resonance position caused by the light is $E_{eg}(\varepsilon_r, I)$. Even at ultralow temperatures on the order of microdegrees Kelvin Doppler broadening and photon recoil can be a significant factor for a narrow resonance with a width of a few kilohertz or less. To include these effects the collision energy ε_r in Eq. (1) should be replaced by $\varepsilon_r + \varepsilon_D - E_{\text{rec,mol}}$, where ε_D is the Doppler shift and $E_{\text{rec,mol}}$ is the energy of the molecule recoiling from a single photon [19].

It is convenient to define a complex scattering length \mathcal{A} [9], which characterizes the variation of the elastic scattering S -matrix element with k_r as $k_r \rightarrow 0$,

$$S_{gg} = \exp[-2i\mathcal{A}(\Delta, I)k_r], \quad (2)$$

where $k_r = \sqrt{2\mu\varepsilon_r}/\hbar$ and μ is the reduced mass of colliding atoms. The length \mathcal{A} can be written as

$$\mathcal{A}(\Delta, I) = a(\Delta, I) - ib(\Delta, I), \quad (3)$$

where the real part

$$a(\Delta, I) = \lim_{k_r \rightarrow 0} - \frac{\text{Im}(S_{gg})}{2k_r} \quad (4)$$

is the scattering length modified by the laser radiation and the imaginary part

$$b(\Delta, I) = \lim_{k_r \rightarrow 0} \frac{1 - |S_{gg}|^2}{4k_r} \quad (5)$$

describes inelastic events in the collision. This inelasticity implies a loss of ground state atoms during the collision. The imaginary part of the complex scattering length is closely related to the atom loss rate coefficient

$$\lim_{k_r \rightarrow 0} \mathcal{K}(\Delta, I) = \lim_{k_r \rightarrow 0} \frac{\pi\hbar}{\mu k_r} (1 - |S_{gg}|^2) = \frac{4\pi\hbar}{\mu} b(\Delta, I). \quad (6)$$

This formulation highlights the modification of basic scattering properties (the scattering length and inelastic collision rate) due to presence of laser radiation.

Following Ref. [10], the terms on the right-hand side of Eqs. (4) and (5) can be written as

$$\begin{aligned} - \frac{\text{Im}(S_{gg})}{2k_r} = & - \frac{\sin(2\eta_g)}{2k_r} \frac{(\Delta + \varepsilon_r - E_{eg} - \Delta_e)^2 + \frac{(\Gamma_{pe}^2 - \Gamma_{eg}^2)}{4}}{(\Delta + \varepsilon_r - E_{eg} - \Delta_e)^2 + \frac{(\Gamma_{pe} + \Gamma_{eg})^2}{4}} \\ & + \frac{\cos(2\eta_g)}{2k_r} \frac{\Gamma_{eg}(\Delta + \varepsilon_r - E_{eg} - \Delta_e)}{(\Delta + \varepsilon_r - E_{eg} - \Delta_e)^2 + \frac{(\Gamma_{pe} + \Gamma_{eg})^2}{4}} \end{aligned} \quad (7)$$

and

$$\frac{1 - |S_{gg}|^2}{4k_r} = \frac{1}{4k_r} \frac{\Gamma_{pe}\Gamma_{eg}}{(\Delta + \varepsilon_r - E_{eg} - \Delta_e)^2 + \frac{(\Gamma_{pe} + \Gamma_{eg})^2}{4}}. \quad (8)$$

Taking the $k_r \rightarrow 0$ limit of Eq. (7) the scattering length is

$$a(\Delta, I) = a_{\text{bg}} + \frac{1}{2} \left(\frac{\Gamma_{eg}}{k_r} \right) \frac{(\Delta - E_{eg} - \Delta_e)}{(\Delta - E_{eg} - \Delta_e)^2 + \frac{\Gamma_{pe}^2}{4}} \quad (9)$$

This limit is obtained by using the $k_r \rightarrow 0$ Wigner threshold behavior in Ref. [10] of the elastic phase shift $\eta_g \sim k_r$, the stimulated width $\Gamma_{eg} \sim k_r$, and the stimulated shift $E_{eg} \sim \text{constant}$ for an s -wave collision [10]. The ground-state s -wave scattering length in the absence of light, the background scattering length, is

$$a_{\text{bg}} = - \lim_{k_r \rightarrow 0} \frac{\eta_g}{k_r}. \quad (10)$$

The scattering length Eq. (9) is the sum of the background scattering length and a length due to the light coupling. The latter length has a dispersive form. Equation (9) has been verified experimentally [11,12]. The imaginary part of the

complex scattering length describing atom loss can be written in the form of a Lorentz distribution

$$b(\Delta, I) = \frac{1}{4} \frac{\Gamma_{pe} \left(\frac{\Gamma_{eg}}{k_r} \right)}{(\Delta - E_{eg} - \Delta_e)^2 + \frac{\Gamma_{pe}^2}{4}}. \quad (11)$$

It should be emphasized that the description of collisions in terms of an energy-independent quantity, the complex scattering length, is possible only if the collision energy is sufficiently small. If the thermal spread in collision energy ε_r is large compared to the natural line width Γ_{pe} , or if there is energy-dependent power broadening where Γ_{eg} is larger than Γ_{pe} for some ε_r , it is necessary to use the full expressions in Eq. (1) or (8) to calculate elastic collision rates or photoassociation line shapes. Since $k_B T/h = 21$ kHz for $T = 1$ μ K, where k_B is Boltzmann's constant, this situation could apply for photoassociation lines near the intercombination transition of cold alkaline-earth-metal atoms. In any case, the key quantities for characterizing the collision are the stimulated width $\Gamma_{eg}(\varepsilon_r, I)$ and shift $E_{eg}(\varepsilon_r, I)$. We now turn our attention to their determination.

III. STIMULATED WIDTH AND SHIFT OF THE RESONANCE

Bohn and Julienne [10] give the following expressions for the stimulated width $\Gamma_{eg}(\varepsilon_r, I)$ and shift $E_{eg}(\varepsilon_r, I)$:

$$\Gamma_{eg}(\varepsilon_r, I) = 2\pi |V_{eg}^{\text{las}}|^2 \left| \int_0^\infty dR \phi_e(R) f_g(R) \right|^2, \quad (12)$$

$$E_{eg}(\varepsilon_r, I) = 2\pi |V_{eg}^{\text{las}}|^2 \int_0^\infty dR \phi_e(R) g_g(R) \int_0^R dR' \phi_e(R') f_g(R'), \quad (13)$$

where the optical coupling term $|V_{eg}^{\text{las}}|^2$ is proportional to the laser intensity. The unit normalized excited-state vibrational wave function, $\phi_e(R)$, is a solution of the Schrödinger equation with excited state potential $V_e(R)$. The energy-normalized scattering wave functions $f_g(R)$ and $g_g(R)$, are the regular and irregular solution of the Schrödinger equation with ground state potential $V_g(R)$ and energy ε_r , respectively. The s -wave functions $f_g(R)$ and $g_g(R)$ have the following form at large R :

$$f_g(R) = \sqrt{\frac{2\mu}{\pi \hbar^2 k_r}} \sin(k_r R + \eta_g), \quad (14)$$

$$g_g(R) = -\sqrt{\frac{2\mu}{\pi \hbar^2 k_r}} \cos(k_r R + \eta_g). \quad (15)$$

It is convenient to rewrite Eqs. (12) and (13) in the form

$$\Gamma_{eg}(\varepsilon_r, I) = \Gamma_A \frac{3}{4\pi} \frac{I \lambda_A^3}{c} f_{\text{rot}}^\Gamma f_{FC}^\Gamma(\varepsilon_r), \quad (16)$$

$$E_{eg}(\varepsilon_r, I) = \Gamma_A \frac{3}{4\pi} \frac{I \lambda_A^3}{c} f_{\text{rot}} f_{FC}^E(\varepsilon_r), \quad (17)$$

which emphasizes the dependence on the laser intensity I , the natural decay width of the atomic transition Γ_A , and the wavelength of the atomic transition λ_A . The bound-free Franck-Condon factor f_{FC}^Γ per unit energy is

$$f_{FC}^\Gamma(\varepsilon_r) = \left| \int_0^\infty dR \phi_e(R) f_g(R) \right|^2 \quad (18)$$

and f_{FC}^E is

$$f_{FC}^E(\varepsilon_r) = \int_0^\infty dR \phi_e(R) g_g(R) \int_0^R dR' \phi_e(R') f_g(R'). \quad (19)$$

Finally, c is speed of light and f_{rot} is a dimensionless rotational line strength factor of order unity.

The light-induced shift can also be calculated using Fano theory [1] of a bound state coupled to a continuum. In such an approach, $f_{FC}^E(\varepsilon_r)$ can be written as [30]

$$f_{FC}^E(\varepsilon_r) = \frac{1}{2\pi} \wp \int_0^\infty d\varepsilon \frac{f_{FC}^\Gamma(\varepsilon)}{\varepsilon_r - \varepsilon} + \frac{1}{2\pi} \sum_g \frac{f_{ge}}{\varepsilon_r - E_g} \quad (20)$$

where \wp denotes a principal part integral over all collision energies, and the sum is over all bound states of the ground electronic potential. The quantity f_{ge} is the bound-bound Franck-Condon factor

$$f_{ge} = \left| \int_0^\infty dR \phi_g(R) \phi_e(R) \right|^2, \quad (21)$$

where $\phi_g(R)$ is a unit normalized ground state vibrational wave function with energy E_g assuming that the potential energy of two separated ground state atoms is zero.

It follows from Eq. (20) that the shift can either be positive or negative as $\varepsilon_r \rightarrow 0$, since the contribution of the principal part integral and the sum have opposite signs. If the first term is larger, the shift will be negative, whereas if the second term is larger, the shift will be positive.

IV. STATIONARY PHASE APPROXIMATION

This section describes the evaluation of the Franck-Condon factors defined by Eqs. (18) and (19) using the stationary phase approximation. The derivation generalizes the reflection approximation given in Ref. [10]. It is convenient to start the derivation by defining the function

$$f_e(R) = \phi_e(R) \sqrt{\frac{\partial n}{\partial E_e}}, \quad (22)$$

where $\partial n / \partial E_e$ is the density of vibrational levels in the excited potential. Following Milne's approach [31,32], we can now write the regular and irregular wave functions of both ground and excited state in the phase-amplitude form

$$f_i(R) = \sqrt{\frac{2\mu}{\pi \hbar^2}} \alpha_i(R) \sin[\beta_i(R)] \quad (23)$$

$$g_i(R) = -\sqrt{\frac{2\mu}{\pi\hbar^2}} \zeta_i(R) \cos[\xi_i(R)], \quad (24)$$

where the index i is g for the ground and e for the excited state, and $\alpha_i(R)$ and $\beta_i(R)$ [$\zeta_i(R)$ and $\xi_i(R)$] denote the amplitude and phase of the regular (irregular) wave functions, respectively. The nonlinear Milne equations (see Refs. [31,32]) can then be solved to find the exact solution of the Schrödinger equation. In general, the amplitude is a slowly varying function of R , while the phase varies by multiple units of π , depending on the depth of the R -dependent molecular potential $V_i(R)$. Note that $\beta_e(R) = \xi_e(R)$ and $\alpha_e(R) = \zeta_e(R)$ for $R \rightarrow \infty$.

The Franck-Condon factor for the stimulated width, Eq. (18), is then

$$f_{FC}^\Gamma = \left(\frac{\partial E_e}{\partial n} \right) \left(\frac{2\mu}{\pi\hbar^2} \right)^2 |I_{eg}|^2, \quad (25)$$

where

$$I_{eg} = \int_0^\infty dR \alpha_e(R) \alpha_g(R) \sin[\beta_e(R)] \sin[\beta_g(R)]. \quad (26)$$

If we neglect the contribution from the fast oscillating term $\cos[\beta_g(R) + \beta_e(R)]$ in I_{eg} , the integral equals

$$I_{eg} \approx \frac{1}{2} \int_0^\infty dR \alpha_e(R) \alpha_g(R) \cos[\beta_g(R) - \beta_e(R)], \quad (27)$$

and can be evaluated by the stationary phase method. The stationary phase method finds that the main contribution to the integral comes from the radial region, where the phase is stationary, i.e., $\frac{\partial}{\partial R}[\beta_g(R) - \beta_e(R)] = 0$. An analytical expression for the integral then crucially relies on an accurate approximation of the phases $\beta_g(R)$ and $\beta_e(R)$ and, thus, the stationary phase point.

The phase of the excited state bound state wave function is well approximated by the semiclassical Wentzel-Kramers-Brillouin (WKB) approximation. In fact, we have $\beta_e(R) = -\pi/4 - \Delta\beta_e(R, R_t)$ for $R < R_t$, where R_t is the classical outer turning point defined as the largest internuclear separation where the local wave number $k_e(R) = \sqrt{2\mu[\Delta_e - V_e(R)]/\hbar^2}$ is zero and $\Delta\beta_e(R, R_t) = \int_R^{R_t} dR' k_e(R')$. The WKB approximation for the amplitude is $\alpha_e(R) = 1/\sqrt{k_e(R)}$ when $R < R_t$.

A similar semi-classical approximation for $\beta_g(R)$ of the scattering solutions at ultracold collision energies cannot be used. For collision energies that lie within the Wigner threshold regime, there is always a range of internuclear separations where the WKB approximation breaks down. For van der Waals potentials for which the long-range form is $-C_6/R^6$, this happens near $R \approx 0.5(2\mu C_6/\hbar^2)^{1/4}$ [5]. Hence, we must use the exact quantum mechanical value for $\beta_g(R)$. Even though the precise value of the ground state phase cannot be determined by the WKB approximation, its derivatives are nonetheless well approximated by this approximation. That is, for example, $\partial\beta_g/\partial R \approx k_g(R)$, where $k_g(R) = \sqrt{2\mu[\varepsilon_r - V_g(R)]/\hbar^2}$ is the local wave number of the ground

state potential. Similarly, the second derivative of $\beta_g(R)$ is proportional to $\partial V_g/\partial R$. We call this approximation of $\beta_g(R)$ “quasi-classical,” as it improves on the semiclassical WKB approximation.

It follows from the approximate expressions for $\beta_g(R)$ and $\beta_e(R)$ that the stationary phase point is equal to the well-known Condon point R_c , defined as the largest internuclear separation at which $k_e(R_c) = k_g(R_c)$ and that $R_c < R_t$. Finally, the phase difference around the Condon point is

$$\beta_g(R) - \beta_e(R) \approx b_0 + b_1(R - R_c) + \frac{b_2}{2}(R - R_c)^2, \quad (28)$$

where

$$b_0 = \beta_g(R_c) + \Delta\beta_e(R_c, R_t) + \frac{\pi}{4}, \quad (29)$$

$$b_1 \approx 0, \quad (30)$$

$$b_2 \approx \frac{\mu D_c}{\hbar^2 k_e(R_c)}, \quad (31)$$

and we have used that $k_e(R_c) = k_g(R_c)$ and

$$D_c = \left. \frac{\partial V_e}{\partial R} \right|_{R_c} - \left. \frac{\partial V_g}{\partial R} \right|_{R_c}. \quad (32)$$

The quasi-classical stationary phase approximation of the integral Eq. (26) now gives [10]

$$\begin{aligned} I_{eg} &\approx \frac{1}{2} \int_0^\infty dR \alpha_e(R) \alpha_g(R) \cos \left[b_0 + \frac{b_2}{2}(R - R_c)^2 \right] \\ &\approx \frac{1}{2} \alpha_e(R_c) \alpha_g(R_c) \sqrt{\frac{2\pi}{b_2}} \cos \left[b_0 + \frac{\pi}{4} \right] \\ &\approx -\sqrt{\frac{\pi\hbar^2}{2\mu D_c}} \alpha_g(R_c) \sin[\beta_g(R_c) + \Delta\beta_e(R_c, R_t)]. \end{aligned} \quad (33)$$

for positive D_c and b_2 . The second line in Eq. (33) follows from evaluating the integral after assuming that the two α factors are slowly varying and can be replaced by their values at $R = R_c$.

The stationary phase approximation is expected to be valid if the quadratic expansion of Eq. (28) applies, in other words, if D_c is sufficiently large that higher order corrections are small. A large D_c implies very different ground and excited state potentials. Equation (33) is similar to that obtained in Ref. [10] and differs only in the definition of b_0 and D_c . That is, $b_0 = \beta_g(R_c) + \pi/4$ is replaced by $b_0 = \beta_g(R_c) + \Delta\beta_e(R_c, R_t) + \pi/4$, and $D_c = \partial V_e/\partial R|_{R_c}$ is replaced by $D_c = \partial V_e/\partial R|_{R_c} - \partial V_g/\partial R|_{R_c}$. Finally, we obtain

$$f_{FC}^\Gamma \approx \frac{\partial E_e}{\partial n} \frac{1}{D_c} |f_g(R_c)|^2 \left| \frac{\sin[\beta_g(R_c) + \Delta\beta_e(R_c, R_t)]}{\sin[\beta_g(R_c)]} \right|^2. \quad (34)$$

This expression reduces to that for the reflection approximation [10] by equating $R_c = R_t$.

Similar to the definition in Eq. (25), the shift in Eq. (19) can be written as

$$f_{FC}^E = \left(\frac{\partial E_e}{\partial n} \right) \left(\frac{2\mu}{\pi\hbar^2} \right)^2 J_{eg}, \quad (35)$$

where the integral J_{eg} is

$$J_{eg} \approx - \int_0^\infty dR \alpha_e(R) \zeta_g(R) \sin[\beta_e(R)] \cos[\xi_g(R)] \\ \times \int_0^R dR' \alpha_e(R') \alpha_g(R') \sin[\beta_e(R')] \sin[\beta_g(R')]. \quad (36)$$

Using the semiclassical stationary phase approximation, we find

$$J_{eg} \approx - \frac{1}{2} \frac{\pi\hbar^2}{2\mu D_c} \alpha_g(R_c) \zeta_g(R_c) \sin[\beta_g(R_c) + \Delta\beta_e(R_c, R_t)] \\ \times \cos[\xi_g(R_c) + \Delta\beta_e(R_c, R_t)]. \quad (37)$$

and thus

$$f_{FC}^E \approx \frac{1}{2} \frac{\partial E_e}{\partial n} \frac{1}{D_c} f_g(R_c) g_g(R_c) \frac{\sin[\beta_g(R_c) + \Delta\beta_e(R_c, R_t)]}{\sin[\beta_g(R_c)]} \\ \times \frac{\cos[\xi_g(R_c) + \Delta\beta_e(R_c, R_t)]}{\cos[\xi_g(R_c)]}. \quad (38)$$

When $R_c = R_t$, Eq. (38) simplifies to the corresponding expression in Ref. [10].

V. RESULTS

We have carried out model calculations for strontium and calcium in order to investigate the ability of the stationary phase approximation to determine the width and shift of photoassociation resonances near the intercombination line of an alkaline-earth atom. The expressions given in the former section work well in the cases where the reflection approximation is applicable. Therefore, our tests are focused on cases in which reflection approximation breaks down. First, we investigate the case of Sr, for which the excited state potential $V_e(R)$ for large R is described by combination of the van der Waals potential and a weak resonant dipole interaction. Second, we investigate the case of Ca for which the excited state potential for large R is described by the van der Waals potential with the dispersion coefficient close to that in the excited state.

A. Strontium

The short-range form of the potentials $V_g(R)$ and $V_e(R)$ for the strontium dimer is insufficiently known to predict the background scattering length of $V_g(R)$ or the binding energy of weakly bound states of $V_e(R)$. However, the density of excited state levels, $\partial E_e / \partial n$, is predominantly governed by the long-range behavior of $V_e(R)$. Since photoassociative spectroscopy is sensitive to weakly bound and the spatially

extended excited state levels, it is sufficient to construct model potentials for both ground and excited state with the correct long-range behavior.

We model the excited state by a Lennard-Jones potential plus a resonant dipole-dipole interaction

$$V_e(R) = \frac{C_{12}^{(e)}}{R^{12}} - \frac{C_6^{(e)}}{R^6} + \frac{C_3^{(e)}}{R^3}, \quad (39)$$

where the values of the parameters are chosen to model the shallow ${}^3\Pi_u$ potential (or more precisely the 0_u^+ potential correlating to the ${}^3P_1 + {}^1S_0$ limit) [33]. In fact,

$$C_3^{(e)} = - \frac{3}{2} \frac{\hbar}{\tau_A} \left(\frac{\lambda_A}{2\pi} \right)^3, \quad (40)$$

where τ_A is the lifetime of the excited atomic 3P_1 state and λ_A is the wavelength of a photon resonant with the transition from the atomic excited state to the 1S_0 ground state. We have used $\lambda_A = 689$ nm, $\tau_A = 21.46$ μ s (compare to Ref. [34]) and the van der Waals coefficient of the excited state $C_6^{(e)} = 3512.8 E_h a_0^6$, which reproduce experimental spectra of 0_u^+ bound obtained for strontium [25]. Here the atomic unit of length is the Bohr radius $a_0 = 0.05291772$ nm and the atomic unit of energy is the Hartree energy $E_h = 4.359744 \times 10^{-18}$ J. The $C_{12}^{(e)}$ coefficient is determined from the relation $C_{12}^{(e)} = [C_6^{(e)}]^2 / (4D^{(e)})$, where the depth of the potential $D^{(e)}$ is chosen to be $D^{(e)}/h = 55082.5$ GHz.

The interaction of two ground state strontium atoms is described by the Lennard-Jones potential

$$V_g(R) = \frac{C_{12}^{(g)}}{R^{12}} - \frac{C_6^{(g)}}{R^6}. \quad (41)$$

We use $C_6^{(g)} = 3170 E_h a_0^6$ from the accurate calculations of Ref. [35]. Moreover, $C_{12}^{(g)} = [C_6^{(g)}]^2 / (4D_e^{(g)})$ with $D_e^{(g)}/h = 32200$ GHz to reproduce roughly the same potential depth as [33] and, more importantly, such that for the ${}^{88}\text{Sr}$ isotope the scattering length of $V_g(R)$ is small and positive with $a_{bg} = 4 a_0$. A recent experimental determination [36] shows that the scattering length for this system has a value between $-1 a_0$ and $13 a_0$.

We begin our analysis of the validity of our stationary phase approximation with a calculation of the Franck-Condon factor Eq. (18) for the width of the photoassociative line. We do this using numerical wave functions of the excited bound states $\phi_e(R)$ and the scattering ground state $f_g(R)$ at energy $\varepsilon_e / k_B = 1$ μ K. The bound and scattering wave functions have been calculated using the Numerov method [37]. For the purpose of testing various approximations, the rotational energy in the excited bound state as well as multichannel coupling are neglected [19]. The ground scattering calculation is carried for s -waves for which the rotational energy is zero. Figure 1 shows the exact $|\Delta_e| \times f_{FC}^E$ (filled circles) as a function of the binding energy Δ_e of each of the last 14 bound states of $V_e(R)$. We plot this dimensionless product of the Franck-Condon factor and the binding energy in all figures of this paper in order to reduce the range of variation on the vertical axis of the figures.

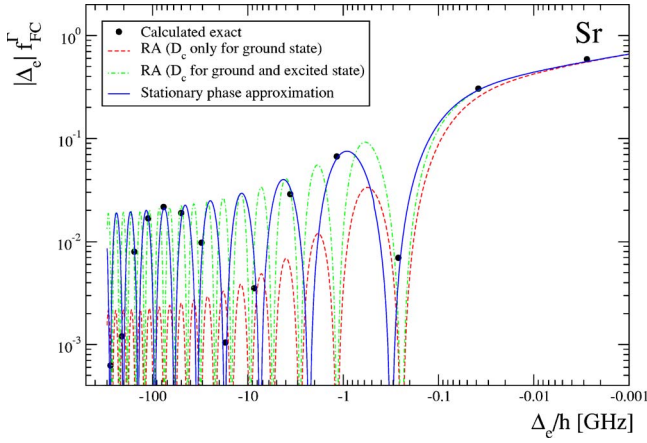


FIG. 1. (Color online) The dimensionless quantity $|\Delta_e| f_{FC}^F$, which is proportional to the light-induced width of a photoassociation line of Sr, as a function of Δ_e . The calculation is for s -wave collisions at an energy of $\varepsilon_r/k_B=1 \mu\text{K}$ assuming a background scattering length of $a_{bg}=4 a_0$.

The exact results are compared to those from approximate analytical formulas from the quasi-classical approach discussed above. These analytical formulas are continuous functions of Δ_e and, consequently, can be shown as curves in the figures. The first approximation is the original reflection approximation (RA) labeled as “RA (D_c only for ground state).” In this approximation, Franck-Condon factors can be calculated from Eq. (34) with $R_t=R_c$, so that the phase difference $\Delta\beta_e(R_c, R_t)=0$, and the slope of $V_g(R)$ is negligible compared to the slope of $V_e(R)$ at the Condon point, i.e., $D_c=\partial V_e/\partial R|_{R_c}$. A second approximation is the reflection approximation with $R_t=R_c$ but now with the complete D_c , which includes the contribution due to the finite slope of the ground state potential. It is labeled as “RA (D_c for ground and excited state).” Finally, the third and most accurate approximation is given by Eq. (34), which takes into account the phase difference between the turning and Condon point and the slopes of both the ground and excited state potentials. This third approximation is labeled as the “Stationary phase approximation.” For all three approximations, the wave function $f_g(R)$ is obtained from the exact numerical scattering solution of the Schrödinger equation of the ground state potential. The phase $\beta_g(R)$ was determined from the nodal pattern of $f_g(R)$ and Eq. (23).

Figure 1 shows that the exact results agree well with results from Eq. (34) for all binding energies. The two versions of the reflection approximation, however, are only applicable for the last few bound states. These latter bound states have large Condon and outer turning points, where the resonant dipole-dipole interaction is large compared to the van der Waals potential. Hence, the calculations show that the phase difference $\Delta\beta_e$ accrued between the turning and Condon point must be taken into account to correctly estimate the stimulated width of a photoassociation resonance in strontium near the intercombination transition. The magnitude of this phase difference can be estimated using the WKB approximation.

Next, we calculate Eq. (19), a factor defining the light-induced shift. To do this we use both regular and irregular

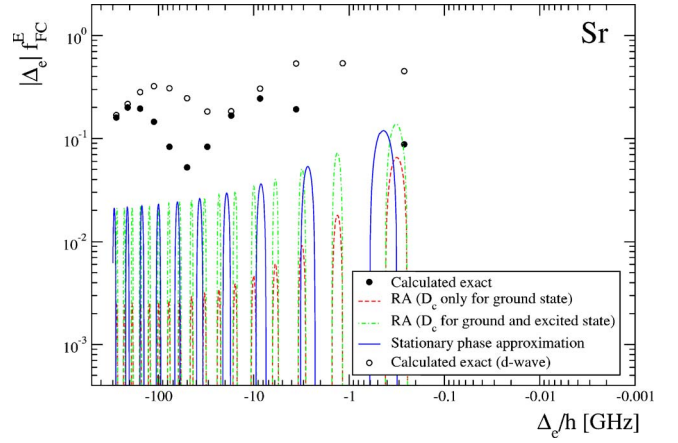


FIG. 2. (Color online) The dimensionless quantity $|\Delta_e|^E f_{FC}^E$, which is proportional to the light-induced shift of a photoassociation line of Sr, as a function of Δ_e . Only bound states with positive shifts are shown. The ground state potential and scattering energy is as in Fig. 1.

solutions of the Schrödinger equation in the ground scattering state at $\varepsilon_r/k_B=1 \mu\text{K}$. The exact values of $|\Delta_e| \times f_{FC}^E$ for bound states with binding energies Δ_e are shown as filled circles in Fig. 2 for positive shifts and in Fig. 3 for negative shifts. Alternatively, f_{FC}^E can be evaluated using the Fano expression of Eq. (20) and, in fact, we find that for the two most weakly bound states f_{FC}^E is completely determined by the principal-part term of Eq. (20). Although Eqs. (19) and (20) are equivalent, it is difficult to get convergence using Eq. (20) because it requires integration over a large range of collision energies.

The exact numerically calculated values of f_{FC}^E can be compared to results from the three approximate analytical formulas as in the discussion of the width of the PA resonances. Figure 3 shows that the exact results are reasonably well approximated by the quasi-classical stationary phase model when the reflection approximation is valid. For more

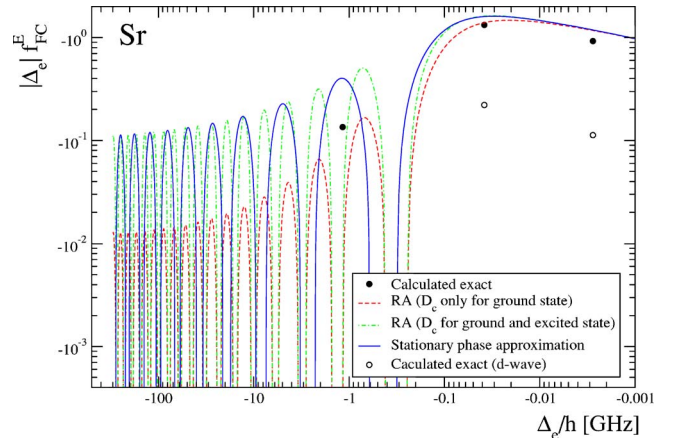


FIG. 3. (Color online) The dimensionless quantity $|\Delta_e|^E f_{FC}^E$, which is proportional to the light-induced shift of a photoassociation line of Sr, as a function of Δ_e . Only bound states with negative shifts are shown. The ground state potential and scattering energy is as in Fig. 1.

TABLE I. The light-induced width Γ_{eg} , shift E_{eg} , and the optical length l_{opt} for near-threshold optical Feshbach resonances for strontium model potentials at a laser intensity $I=1 \text{ W/cm}^2$ and collision energy $\varepsilon_r/k_B=1 \text{ } \mu\text{K}$.

Δ_e/h (GHz)	Γ_{eg}/h (MHz)		E_{eg}/h (MHz)		l_{opt}/a_0
	<i>s</i> -wave	<i>d</i> -wave	<i>s</i> -wave	<i>d</i> -wave	
-3.592	0.0002	1.9×10^{-10}	+0.0016	+0.0044	11
-1.167	0.0017	1.2×10^{-9}	-0.0034	+0.0135	79
-0.264	0.0008	2.2×10^{-10}	+0.0097	+0.0499	36
-0.038	0.2346	2.5×10^{-7}	-1.0161	-0.1691	1.1×10^4
-0.003	6.2059	2.7×10^{-4}	-9.7463	-1.1867	2.9×10^5

deeply bound states shown in both Figs. 2 and 3, however, none of the three approximate models reproduce the exact calculation of the integrals in Eq. (19).

Thus far, we have only considered *s*-wave scattering. The light also couples *d*-wave scattering states to the same excited bound state of the 0_u^+ molecular potential [19]. This *d*-wave ground scattering state is a solution of the potential $V_g(R)+6\hbar^2/(2\mu R^2)$. The *d*-wave Franck-Condon factor for the width is typically negligible compared to the *s*-wave Franck-Condon factor for temperatures in the microdegrees Kelvin range. On the other hand, however, the shift due to coupling of the excited state to *d*-wave collisions can be significant. Consequently, we have carried out calculations of the *d*-wave contributions to the shift. They are shown in Figs. 2 and 3, assuming that the *s*-wave and *d*-scattering states are coupled to the same excited bound state. The *d*-wave shifts can have a similar size as the *s*-wave shifts.

In order to illustrate typical magnitudes, Table I lists the exact *s*-wave and *d*-wave width Γ_{eg} and shift E_{eg} at a single laser intensity and collision energy for the last five bound states below threshold. It must be emphasized that these results should not be directly compared to experiments, since only a single channel model of the excited bound states is used, and the rotational energy in the excited state is neglected. Nevertheless, the calculation illustrates the expected order of magnitude of the parameters.

Optical control of strontium scattering properties and, thus, control of the scattering length, Eq. (9), is well characterized by the optical length [9,29]

$$l_{\text{opt}} = \frac{\Gamma_{eg}}{2k_r\Gamma_{pe}}. \quad (42)$$

An optical length that is large compared to a_{bg} indicates that control will be feasible. Table I lists l_{opt} for $I=1 \text{ W/cm}^2$. We have assumed that $\Gamma_{pe}=2\Gamma_A$, where $\Gamma_A=7.5 \text{ kHz}$ for the intercombination line of strontium, and that it is the same for all the bound states. From the Table I, it follows that l_{opt} is large compared to the background scattering length of ^{88}Sr . In the first experimental demonstration of optical control of the scattering length in a rubidium Bose-Einstein condensate [12], an optical length as large as $100 a_0$ was reached. However, for rubidium the laser power was a few hundred times bigger than that used to calculate l_{opt} in Table I and optically

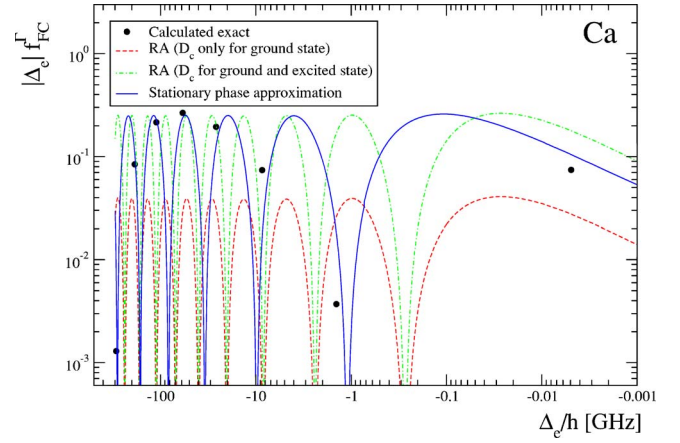


FIG. 4. (Color online) The dimensionless quantity $|\Delta_e|J_{FC}^F$, which is proportional to the light-induced width of a photoassociation line of Ca, as a function of Δ_e . The calculation is for *s*-wave collisions at an energy of $\varepsilon_r/k_B=1 \text{ } \mu\text{K}$ assuming a background scattering length of $a_{bg}=390 a_0$.

induced losses associated with on-resonant driving of the rubidium excited state only allowed the scattering length to be changed for a very short time. Strontium is much more attractive in this regard, in that l_{opt} is large enough that losses could be suppressed by detuning from resonance while still allowing optical control for much longer time intervals at reasonable laser intensity [25]. A similar situation can also be expected in ytterbium, which has been shown to undergo Bose-Einstein condensation [20]. Clearly species with intercombination line transitions are promising candidates for optical control of degenerate quantum gases; for example, see Ref. [38].

B. Calcium

The interaction potentials of calcium are like in strontium insufficiently well known to be predictive. Hence, we are forced to use model potentials. In this case, however, the contribution of the resonant dipole-dipole interaction in the excited state is negligible because of the long lifetime of the 3P_1 atomic state. Therefore, we use $C_3^{(e)}=0$ and both ground and excited state potentials are Lennard-Jones potential. For the excited state $V_e(R)$ models the $^3\Pi_u$ potential of Ca [39,40], with $C_6^{(e)}=2462 E_h a_0^6$ [19,41] and $D_6^{(e)}/h=44075 \text{ GHz}$. The ground state potential has $C_6^{(g)}=2081 E_h a_0^6$ as determined by Allard *et al.* [42] and $D_6^{(g)}/h=31848.4 \text{ GHz}$ is chosen to get a relatively large positive scattering length $a_{bg}=390 a_0$ [42]. Note that the difference between ground and excited state van der Waals coefficients is almost two times smaller for calcium than for strontium.

Figure 4 shows the width of a photoassociation line near the Ca intercombination transition. Results for the exact expression as well as the quasi-classical estimates are shown. It is clear that the stationary phase approximation is not as accurate as for Sr. This is mainly because the ground and excited states have a similar van der Waals potentials. The assumptions needed by a stationary phase approximation fail for such a case.

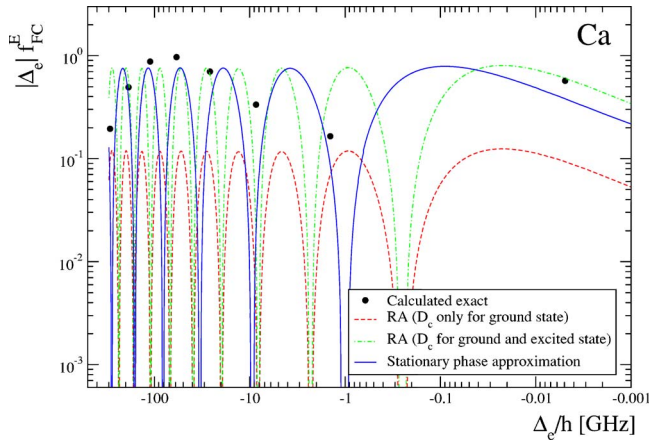


FIG. 5. (Color online) The dimensionless quantity $|\Delta_e| f_{FC}^E$, which is proportional to the light-induced shift of a photoassociation line of Ca, as a function of Δ_e . For our calcium potentials the shift for the bound states of $V_e(R)$ is positive. For the approximate calculations only positive f_{FC}^E are shown. The ground state potential and scattering energy is as in Fig. 4.

We have also carried out calculations of the Franck-Condon factors for the light-induced shift. The results of these calculations are presented in Fig. 5. For our calcium potentials, the exact shift is always positive. It turns out to be a consequence of the large bound-bound contribution to the shift in the Fano expression Eq. (20). This is in agreement with results obtained previously [19].

A comparison of the exact results to the quasi-classical approximation is again far from perfect. Nevertheless, the quasi-classical expression allows us to give bounds on the shift. It also confirms that for our Ca potentials the shift for s -wave collisions is positive. The quasi-classical approximation only predicts a negative shift for narrow binding-energy regions. No bound states of $V_e(R)$ occur for such binding energies.

VI. DISCUSSION

The calculations for calcium shows that even the improved expression for the light-induced width shows some discrepancies compared to the exact results. This is a manifestation of the well-known fact that the stationary phase approximation breaks down when the potentials in the ground and excited states are too similar, as in the test case in which the difference between $C_6^{(e)}$ and $C_6^{(g)}$ is not more than 20%. However, even in this case, the stationary phase approximation, Eq. (34) correctly predicts the nodes of the Franck-Condon factor f_{FC}^E , whereas the reflection approximations incorrectly predicts the nodal positions over the investigated detuning range.

The stationary phase approximation for the light-induced width gives good results if there is even a small addition of resonance dipole interaction in the excited state. It was clearly demonstrated by the strontium example, for which the approximation in Eq. (34) agrees with the exact results for the full detuning range investigated. By contrast, the ordinary reflection approximation breaks down for levels with

binding energies larger than 0.1 GHz, where the van der Waals interaction start to dominate. The stationary phase approximation also becomes better as the difference between dispersion coefficients in the ground and excited state increases. We have tested this with the calcium example by changing $C_6^{(e)}$. It was found that for $C_6^{(e)} \geq 3C_6^{(g)}$, the light-induced widths calculated exactly and with the stationary phase approximation compare to similar good quality, as that shown for the strontium example.

The situation is different in the case of the light-induced shift. The expression, Eq. (38), does not give better results than the ordinary reflection approximation. Some explanation of this fact can be found, taking into account that Eq. (38) very well approximates the following integral

$$\frac{1}{2} \int_0^\infty dR \phi_e(R) g_g(R) \int_0^\infty dR' \phi_e(R') f_g(R'). \quad (43)$$

instead of Eq. (19). This integral in the general case differs from Eq. (19). Therefore, we get no agreement between the results calculated from the exact Eq. (19) and the approximation Eq. (38). On the other hand, for conditions where the reflection approximation can be applied, the integral given by Eq. (43) well approximates Eq. (19), and the exact results can be described by the analytical expressions discussed above.

Clearly, Eq. (34) has a wider range of applicability than the ordinary reflection approximation in describing the Franck-Condon factor needed for the light-induced width. We have shown that this improved approximation can be applied to a system where the reflection approximation fails, in which the interaction in the excited state is described by the combination of the van der Waals potential and a weak resonance interaction. Besides Sr, this approximation could find applications for Ba, Yb, and other systems with similar electronic structure. Moreover, Eq. (34) will give good results when the ratio of $C_6^{(e)}$ and $C_6^{(g)}$ is order of a few or greater. While the reflection approximation does not work well for such a case, the stationary phase approximation gives good results. As an example, a large range of dispersion coefficients can be found in various mixtures of two different alkali-metal species [43]. It was found for such systems [44] that reflection approximation predictions [45] disagree with exact calculations.

VII. CONCLUSION

Although the reflection approximation is useful for calculating light-induced shifts and widths of photoassociation lines for systems where the excited state potential is dominated by a long-range resonant dipole-dipole interaction, we have shown that this approximation fails when both the ground and excited states have similar long-range behavior. We use approximate model potentials to investigate extensions of the quasi-classical stationary phase approximation to situations where both the ground and excited state potentials are predominately determined by a van der Waals interaction.

Our results demonstrate that the light-induced width of the photoassociation resonance can be well described by the

stationary phase approximation over a much wider range of conditions than the reflection approximation. However, the stationary phase approximation does not work as well if the potentials in ground and excited states are similar. This is the case, for example, if the long-range potentials in both ground and excited states have the same C_q/R^q form and the C_q coefficients have similar values. The quasi-classical expressions do not offer any advantage over the reflection approximation for the light-induced shift. Although the conclusions are based on models for the intercombination transitions in alkaline-earth-metal systems, we expect them to apply equally well to allowed transition of mixtures of two differ-

ent alkali-metal species, since these systems are also characterized by van der Waals potentials for the ground and excited state.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to A. Derevianko for making his calculations of dispersion coefficients available before publication. This work has been partially supported by the U.S. Office of Naval Research. The research is part of the program of the National Laboratory FAMO in Toruń, Poland.

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