

## Scattering properties of weakly bound dimers of fermionic atoms

D. S. Petrov,<sup>1,2,3</sup> C. Salomon,<sup>4</sup> and G. V. Shlyapnikov<sup>2,3,5,6</sup>

<sup>1</sup>*ITAMP, Harvard-Smithsonian Center for Astrophysics, and Harvard-MIT Center for Ultracold Atoms, Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA*

<sup>2</sup>*Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California 93106-4030, USA*

<sup>3</sup>*Russian Research Center Kurchatov Institute, Kurchatov Square, 123182 Moscow, Russia*

<sup>4</sup>*Laboratoire Kastler-Brossel, Ecole Normale Supérieure, 24 rue Lhomond, 75005 Paris, France*

<sup>5</sup>*Laboratoire Physique Théorique et Modèles Statistique, Université Paris Sud, Bâtiment 100, 91405 Orsay, France*

<sup>6</sup>*Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65/67, 1018 XE Amsterdam, The Netherlands*

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We consider weakly bound diatomic molecules (dimers) formed in a two-component atomic Fermi gas with a large positive scattering length for the interspecies interaction. We develop a theoretical approach for calculating atom-dimer and dimer-dimer elastic scattering and for analyzing the inelastic collisional relaxation of the molecules into deep bound states. This approach is based on the single-channel zero-range approximation, and we find that it is applicable in the vicinity of a wide two-body Feshbach resonance. Our results draw prospects for various interesting manipulations of weakly bound dimers of fermionic atoms.

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### I. INTRODUCTION

The studies of degenerate atomic Fermi gases attract a great deal of interest as they are directed to reveal novel macroscopic quantum states and provide links between quantum gases and condensed matter systems. Experiments with ultracold two-component clouds of fermionic atoms widely use Feshbach resonances for the intercomponent interaction (scattering length  $a$ ). This allows one to switch the sign and tune the absolute value of  $a$  which at resonance changes from  $+\infty$  to  $-\infty$ . On the positive side of the resonance ( $a > 0$ ), one expects the formation of weakly bound diatomic molecules, which represent composite bosons and can form a Bose-Einstein condensate (BEC). On the negative side ( $a < 0$ ), the interaction between atoms of different components is attractive and they should undergo the well-known Bardeen-Cooper-Schrieffer (BCS) superfluid pairing at sufficiently low temperatures. The BCS transition temperature is much lower than the Fermi energy, which makes it difficult to achieve this transition.

Molecular BEC for  $a > 0$  and atomic BCS pairing for  $a < 0$  describe the system sufficiently far from the resonance. In the vicinity of the resonance, where the density and the scattering length satisfy the inequality  $n|a|^3 \gtrsim 1$ , the gas enters a strongly interacting regime. This BCS-BEC crossover regime has been discussed in the literature in the context of superconductivity [1–4] and for superfluidity in two-dimensional <sup>3</sup>He films [5,6]. Atomic Fermi gases in the strongly interacting regime are expected to have a comparatively high superfluid transition temperature [7–11] and are characterized by a universal behavior of interactions [12–15] and a universal thermodynamics [16]. They are now actively being studied in relation to the nature of superfluid pairing [17–24].

Recent investigations of two-component <sup>40</sup>K and <sup>6</sup>Li atomic Fermi gases are marked by remarkable achievements. Those include the formation [25–28] and Bose-Einstein con-

densation [29–33] of long-lived weakly bound diatomic molecules (dimers) on the positive side of a Feshbach resonance ( $a > 0$ ), and a BEC-type behavior of fermionic atom pairs in the strongly interacting regime [34,35]. An anomalous dependence of frequencies and damping rates of quadrupole excitations on the interaction strength, observed in experiments [36,37], may be a signature for a transition from a superfluid to collisionless regime. Strong evidence for the superfluid regime was obtained in the Innsbruck experiment [38] through the radio-frequency measurement of the pairing gap for a strongly interacting Fermi gas of <sup>6</sup>Li.

The studies of the strongly interacting regime for the BCS-BEC crossover require knowledge of many-body correlations. In particular, one should reproduce a correct equation of state in the limit of BEC of a weakly interacting gas of dimers for  $a > 0$  (see [23]).

Hence, one should know the interaction between these dimers. For a large  $a$ , they are weakly bound and have a large size ( $\sim a$ ) which greatly exceeds the characteristic radius of interaction between the atoms. In our previous work [39], we have outlined a method for studying the elastic interaction between such molecules and their collisional relaxation to deep bound states. This method is based on the zero-range approximation, and the dimer-dimer scattering length is found to be  $0.6a$ . The imaginary part of the scattering amplitude, originating from the collisional relaxation, is extremely small. Being in the highest rovibrational state, these diatomic molecules are characterized by a remarkable collisional stability. The physical reason is the Pauli principle in combination with a large size of the molecular state (small momenta of bound fermionic atoms): collisional relaxation is suppressed as it requires at least two identical fermions with small momenta to approach each other to a short distance [39].

In this paper, we present a detailed analysis of elastic and inelastic atom-dimer and dimer-dimer interactions in the zero-range approximation. The paper is organized as follows.

In Sec. II we introduce the zero-range approximation in a way it has been done for the two-body problem (see, for example, [40,41]). Section III contains a general description of the zero-range approximation for the case of three particles. In Sec. IV, we review the problem of atom-dimer elastic scattering in the zero-range approximation, and in Sec. V, we present a derivation for the relaxation of the dimers to deep bound states in atom-dimer collisions. Sections VI and VII contain a generalization of the zero-range approximation to the case of four particles. In these sections, we present a detailed derivation of the results for the elastic dimer-dimer interaction and for the relaxation of the dimers to deep bound states in dimer-dimer collisions. In Sec. VIII, we show that our results can be used for weakly bound diatomic molecules obtained in two-component atomic Fermi gases by using wide Feshbach resonances, and in Sec. IX we conclude.

## II. ZERO-RANGE APPROXIMATION FOR THE TWO-BODY PROBLEM

We first follow well known results and introduce the zero-range approximation as this has been done for the two-body problem (see [40,41]). We consider elastic pair collisions between cold distinguishable atoms interacting with each other via a spherically symmetric potential and assume that their de Broglie wavelength is much larger than the characteristic radius of this potential,  $R_e$ . In other words, we have the condition  $kR_e \ll 1$ , where  $k$  is the relative wave vector of the atoms. In this case, the scattering is dominated by the  $s$ -wave contribution. The behavior of the wave function at interatomic distances  $r \gg R_e$  is governed by the scattering length  $a$  which is related to the scattering phase shift as  $\delta = -\arctan(ka)$ . Given the scattering length, the details of the interatomic potential at distances  $r \lesssim R_e$  are practically irrelevant for scattering parameters and give rise to corrections of the order of  $kR_e$  or smaller for the scattering amplitude [42].

The key idea of the zero-range approximation is to solve the equation for the free relative motion of two atoms placing the Bethe-Peierls boundary condition on the wave function at a vanishing  $r$ ,

$$\frac{(r\psi)'}{r\psi} = -\frac{1}{a}, \quad r \rightarrow 0, \quad (1)$$

which can also be rewritten as

$$\psi \propto (1/r - 1/a), \quad r \rightarrow 0. \quad (2)$$

One then gets a correct expression for the wave function at distances  $r \gg R_e$ .

For the free relative motion of two colliding atoms, the Schrödinger equation takes the form

$$-(\nabla_{\mathbf{r}}^2 + k^2)\psi = 0. \quad (3)$$

A general solution of this equation for our scattering problem, which is valid at any finite  $r$ , is given by

$$\psi = \exp(i\mathbf{k} \cdot \mathbf{r}) + hG(\mathbf{r}, 0), \quad (4)$$

where  $G(\mathbf{r}, \mathbf{r}') = (1/4\pi|\mathbf{r} - \mathbf{r}'|)\exp(ik|\mathbf{r} - \mathbf{r}'|)$  is the Green function representing the solution of Eq. (3) with the right-

hand side equal to  $\delta(\mathbf{r} - \mathbf{r}')$ . The  $s$ -wave part of the incident wave given by the first term on the right-hand side of Eq. (4) is equal to  $\sin kr/kr$ . As the wave function  $\psi$  should satisfy the boundary condition (1) at  $r \rightarrow 0$ , for the coefficient  $h$  we immediately obtain

$$h = -\frac{a}{1 + ika} = \frac{\exp(2i\delta) - 1}{2ik}. \quad (5)$$

Then Eq. (4) reproduces the well-known result for the  $s$ -wave part of the wave function at  $r \gg R_e$ ,

$$\psi \propto \frac{\sin(kr + \delta)}{kr}. \quad (6)$$

The use of the zero-range approximation is especially important for the case of resonance scattering characterized by the scattering length  $|a| \gg R_e$ . Then, for interparticle distances in the interval  $R_e \ll r \ll 1/k$ , from Eq. (6) one finds that Eq. (2) gives a correct result for  $\psi$  at distances of the order of or even much smaller than  $|a|$ .

For a large positive scattering length  $a \gg R_e$ , there is a weakly bound state of two atoms. The binding energy  $\varepsilon_0$  and wave function  $\phi_0$  of this state at distances  $r \gg R_e$  can also be found in the zero-range approximation.

The free relative motion of atoms in the bound state is described by the Schrödinger equation,

$$(-\nabla_{\mathbf{r}}^2 + m\varepsilon_0/\hbar^2)\phi_0 = 0, \quad (7)$$

where  $m$  is the atom mass, and the (negative) energy of the molecular state is  $E = -\varepsilon_0$ . A general solution of Eq. (7) at any finite  $r$  can be written as

$$\phi_0(r) = \psi_0(\mathbf{r}) + h_0 G_{\varepsilon_0}(\mathbf{r}, 0), \quad (8)$$

where  $G_{\varepsilon_0}(\mathbf{r}, \mathbf{r}') = (1/4\pi|\mathbf{r} - \mathbf{r}'|)\exp(-\sqrt{m\varepsilon_0/\hbar^2}|\mathbf{r} - \mathbf{r}'|)$  is the Green function of Eq. (7), and  $\psi_0$  is the solution of this equation that is finite and regular at any distance including  $r=0$ . For  $r \rightarrow 0$ , the wave function (8) should satisfy the boundary condition (1).

One can easily see that any nontrivial solution of Eq. (7), finite at  $r \rightarrow \infty$ , behaves as  $1/r$  for  $r \rightarrow 0$ . Therefore, we have  $\psi_0=0$ . Then, using the boundary condition (1) for  $\phi_0(r)$  at vanishing  $r$ , one finds that the binding energy of the weakly bound state is

$$\varepsilon_0 = \hbar^2/ma^2, \quad (9)$$

and the wave function  $\phi_0$  normalized to unity is given by

$$\phi_0(r) = (1/\sqrt{2\pi ar})\exp(-r/a). \quad (10)$$

Note that under the condition  $|a| \gg R_e$ , the main contribution to the normalization integral comes from distances  $r \gg R_e$ , where Eq. (10) is valid. Relative corrections to the binding energy  $\varepsilon_0$  are of the order of  $(R_e/a)$ .

## III. GENERAL FORMALISM FOR THREE FERMIONS

Theoretical studies of the three-body problem have a long prehistory (see [43] for a review). In this section, we consider a three-body system consisting of two identical fermi-

ons interacting with a third one, which is not identical to the first two, via a short-range pair isotropic potential  $U(r)$ . The fermions have the same mass and we will denote the identical ones by the symbol  $\uparrow$  and the third one by the symbol  $\downarrow$ . In the center-of-mass reference frame, the state of the system with total energy  $E$  is described by the Schrödinger equation

$$\left[ -\nabla_{\mathbf{x}}^2 - \nabla_{\mathbf{y}}^2 + \sum_{\pm} U\left(\frac{\sqrt{3}\mathbf{x} \pm \mathbf{y}}{2}\right) - E \right] \Psi = 0, \quad (11)$$

where  $\mathbf{y}$  is the distance between the identical fermions, and  $\sqrt{3}\mathbf{x}/2$  is the distance between their center of mass and the third atom. Hereinafter, we use notations in which  $\hbar=m=1$ .

The wave function  $\Psi$  is antisymmetric with respect to the permutation of identical fermions, i.e., it changes sign under the transformation  $\mathbf{y} \rightarrow -\mathbf{y}$ .

We will discuss the case of resonant two-body interaction, that is, we assume that the two-body problem for the interaction potential  $U(r)$  is characterized by a large scattering length

$$|a| \gg R_e. \quad (12)$$

As has been shown by Efimov [44], in this case short-range physics is not important and the three-body problem is universal in the sense that it can be described in terms of the two-body scattering length. One can then use the zero-range approximation for the interatomic potential. This was first done even earlier by Skorniakov and Ter-Martirosian [45] in relation to the neutron-deuteron scattering, which is similar to elastic scattering of atoms by weakly bound dimers. The work of Ref. [45] was followed by related discussions [46]. In this section, we present the form of the zero-range approximation for three-body systems that was outlined in Refs. [39,47] for the three-body recombination and atom-dimer scattering.

Under the condition (12), the zero-range approximation is applicable even at interparticle distances much smaller than  $|a|$ , as long as these distances greatly exceed  $R_e$ . Also, this approximation properly describes weakly bound states of two particles at  $a > 0$ . According to the zero-range approximation, Eq. (11) is equivalent to the Poisson equation

$$-[\nabla_{\mathbf{x}}^2 + \nabla_{\mathbf{y}}^2 + E]\Psi = 0, \quad (13)$$

with the boundary condition (2) set for a vanishing distance between any of the two distinguishable fermions, i.e., for  $\mathbf{r}_{\pm} = (\sqrt{3}\mathbf{x} \pm \mathbf{y})/2 \rightarrow 0$ . Taking into account the symmetry, we can write the boundary conditions at the two boundaries as

$$\Psi \approx \pm \frac{1}{4\pi} f(\mathbf{r}) \left( \frac{1}{r_{\pm}} - \frac{1}{a} \right), \quad r_{\pm} \rightarrow 0, \quad (14)$$

where  $\mathbf{r} = \mp 2\mathbf{y}/\sqrt{3}$  for  $r_{\pm} \rightarrow 0$ . The function  $f$  contains information about the relative motion of a  $\uparrow$ -fermion with respect to the two other atoms when they are on top of each other. In the case of atom-dimer scattering, the function  $f$  plays a role of the wave function of the atom-dimer relative motion.

The Green function of Eq. (13), which is the solution of this equation with the right-hand side equal to  $\delta(\mathbf{x}-\mathbf{x}')\delta(\mathbf{y}-\mathbf{y}')$ , is given by

$$G_E(X) = \begin{cases} -(8\pi^3 X^2)^{-1} EK_2(\sqrt{-EX}), & E < 0, \\ i(16\pi^2 X^2)^{-1} EH_2(\sqrt{EX}), & E > 0. \end{cases} \quad (15)$$

Here  $X = \sqrt{(\mathbf{x}-\mathbf{x}')^2 + (\mathbf{y}-\mathbf{y}')^2}$ ,  $K_2$  is an exponentially decaying Bessel function, and  $H_2$  is a Hankel function representing an outgoing wave. For  $\sqrt{|E|}X \ll 1$ , we have

$$G_0 = (4\pi^3 X^4)^{-1}. \quad (16)$$

As in the two-body case described by Eqs. (4) and (8), a general solution of Eq. (13) at finite distances between  $\uparrow$  and  $\downarrow$  fermions can be expressed through the Green function  $G_E$  (15), with coordinates  $\mathbf{x}'$ ,  $\mathbf{y}'$  corresponding to a vanishing distance between distinguishable fermions, that is, for  $\mathbf{r}'_{\pm} \rightarrow \mathbf{0}$  and for  $\mathbf{r}'_{-} \rightarrow \mathbf{0}$ . We thus have

$$\begin{aligned} \Psi(\mathbf{x}, \mathbf{y}) = & \Psi_0(\mathbf{x}, \mathbf{y}) \\ & + \int G_E[\sqrt{(\mathbf{x}-\mathbf{r}'/2)^2 + (\mathbf{y} + \sqrt{3}\mathbf{r}'/2)^2}] h(\mathbf{r}') d^3 r' \\ & - \int G_E[\sqrt{(\mathbf{x}-\mathbf{r}'/2)^2 + (\mathbf{y} - \sqrt{3}\mathbf{r}'/2)^2}] h(\mathbf{r}') d^3 r', \end{aligned} \quad (17)$$

where  $\Psi_0$  is a properly symmetrized and finite solution of Eq. (13), regular at vanishing distances between  $\uparrow$  and  $\downarrow$  fermions. For a negative total energy  $E$ , nontrivial solutions of this type do not exist and we have to put  $\Psi_0=0$ . The function  $h(\mathbf{r})$  has to be determined relying on the boundary conditions (14).

For this purpose, we consider the limit  $\mathbf{r}_{\pm} \rightarrow \mathbf{0}$  and analyze the leading behavior of the terms on the right-hand side of Eq. (17). The argument of the Green function in the third term can be written as  $\sqrt{r^2 + r'^2 + \mathbf{r} \cdot \mathbf{r}' - \sqrt{3}\mathbf{r}_{\pm} \cdot \mathbf{r}' + r_{\pm}^2}$ , where  $\mathbf{r} = (\mathbf{x} - \sqrt{3}\mathbf{y})/2$ , and this term is finite for  $r_{\pm} \rightarrow 0$ . It can be written as

$$\int G_E(\sqrt{r^2 + r'^2 + \mathbf{r} \cdot \mathbf{r}'} ) h(\mathbf{r}') d^3 r'. \quad (18)$$

In the second term, the argument of the Green function takes the form  $\sqrt{(\mathbf{r}-\mathbf{r}')^2 + r_{\pm}^2}$ . We then subtract from this term and add to it an auxiliary quantity

$$h(\mathbf{r}) \int G_E[\sqrt{(\mathbf{r}-\mathbf{r}')^2 + r_{\pm}^2}] d^3 r' = (1/4\pi r_{\pm}) h(\mathbf{r}) \exp(-\sqrt{-E}r_{\pm}). \quad (19)$$

The result of the subtraction gives a quantity  $I = \int G_E[\sqrt{(\mathbf{r}-\mathbf{r}')^2 + r_{\pm}^2}] [h(\mathbf{r}') - h(\mathbf{r})] d^3 r'$ . For  $r_{\pm} \rightarrow 0$ , this quantity remains finite and can be written as

$$I = P \int G_E(|\mathbf{r}-\mathbf{r}'|) [h(\mathbf{r}') - h(\mathbf{r})] d^3 r', \quad (20)$$

where the symbol P denotes the principal value for the integration over  $dr'$ . The derivation of Eq. (20) and the proof of the convergence of the integral on the right-hand side of this equation are given in the Appendix.

Neglecting terms that are vanishing for  $r_+ \rightarrow 0$ , the two last lines of Eq. (17) are given by the sum of Eqs. (18), (19), and (20). Thus, in the limit  $r_+ \rightarrow 0$  we can write Eq. (17) in the form containing a singular term proportional to  $r_+^{-1}$ , and regular terms independent of  $r_+$ ,

$$\Psi \approx \frac{r_+^{-1} - \sqrt{-E}}{4\pi} h(\mathbf{r}) + \int \{G_E(|\mathbf{r} - \mathbf{r}'|)[h(\mathbf{r}') - h(\mathbf{r})] - G_E(\sqrt{r^2 + r'^2 + \mathbf{r} \cdot \mathbf{r}'} )h(\mathbf{r}')\} d^3 r' + D(\mathbf{r})/4\pi, \quad (21)$$

where  $D(\mathbf{r}) = 4\pi\Psi_0(+\mathbf{r}/2, -\sqrt{3}\mathbf{r}/2)$ , and  $\sqrt{-E} = -i\sqrt{E}$  for positive energies  $E$ . Hereafter we omit the principal value symbol  $P$  for the first term of the integrand of Eq. (21).

As Eq. (21) should coincide with Eq. (14) at  $r_+ \rightarrow 0$ , comparing the singular terms of these equations we immediately find that  $h(\mathbf{r}) = f(\mathbf{r})$ . Matching the regular terms yields the equation for the function  $f$ ,

$$(\hat{L}_E - a^{-1} + \sqrt{-E})f(\mathbf{r}) = D(\mathbf{r}), \quad (22)$$

where the integral operator  $\hat{L}_E$  is given by

$$\hat{L}_E f(\mathbf{r}) = 4\pi \int \{G_E(|\mathbf{r} - \mathbf{r}'|)[f(\mathbf{r}) - f(\mathbf{r}')] + G_E(\sqrt{r^2 + r'^2 + \mathbf{r} \cdot \mathbf{r}'} )f(\mathbf{r}')\} d^3 r'. \quad (23)$$

The operator on the left-hand side of Eq. (22) conserves angular momentum. Therefore, one can expand  $f$  and  $D$  in spherical harmonics and work only with a set of uncoupled equations for functions of a single variable  $r$ . The knowledge of the function  $f(\mathbf{r})$  allows one to calculate all scattering parameters. In the next section, we demonstrate this by calculating the atom-dimer scattering length in the ultracold limit.

#### IV. ATOM-DIMER ELASTIC SCATTERING

According to the discussion in Sec. II, for a large positive scattering length  $a \gg R_e$  one has a weakly bound molecular state of two distinguishable fermions ( $\uparrow$  and  $\downarrow$ ), with the binding energy  $\varepsilon_0 = 1/a^2$  and the wave function  $\phi_0$  described by Eq. (10). We now consider elastic collisions of these bosonic dimers with  $\uparrow$  (or  $\downarrow$ ) fermionic atoms at collision energies  $\varepsilon < \varepsilon_0$ . Then the total energy of the three-body atom-dimer system is  $E = (\varepsilon - \varepsilon_0) < 0$  and collisions do not lead to dissociation of the dimers.

From Eq. (10), one finds that the size of the weakly bound molecular state is  $\sim a$ . For a large separation between the atom and the dimer, the three-body wave function factorizes into a product,

$$\Psi(\mathbf{x}, \mathbf{y}) \approx \phi_0(r_+) \chi(\mathbf{r}), \quad r \gg a. \quad (24)$$

A characteristic value of the distance  $r_+$  between atoms in the dimer is  $\sim a$ , and in the limit  $r \gg a$  the atom-dimer separation is equal to  $\sqrt{3}r/2$ . The wave function  $\chi(\mathbf{r})$  describes the relative atom-dimer motion and can be represented as a superposition of an incident and scattered wave. For  $r \rightarrow \infty$ , we have

$$\chi(\mathbf{r}) \approx \exp(ikz) + \frac{2F(k, \theta) \exp(ikr)}{\sqrt{3} r}, \quad (25)$$

where  $z$  is the direction of incidence,  $\theta$  is the scattering angle, the relative wave vector is defined as  $2k/\sqrt{3}$ , and  $F(k, \theta)$  is the scattering amplitude.

For  $r_+ \rightarrow 0$ , we have

$$\phi_0(r_+) \rightarrow \frac{1}{\sqrt{2\pi a}} \left( \frac{1}{r_+} - \frac{1}{a} \right).$$

Then, comparing  $\Psi$  (24) with Eq. (14), we obtain a relation between the functions  $\chi$  and  $f$ ,

$$\chi(\mathbf{r}) = \sqrt{a/8\pi} f(\mathbf{r}). \quad (26)$$

As we commented in Sec. III, for  $E < 0$  we have to put  $\Psi_0 = 0$  in Eq. (17). This leads to  $D(\mathbf{r}) = 0$ , and Eq. (22) takes the form

$$(\hat{L}_E - a^{-1} + \sqrt{-E})f(\mathbf{r}) = 0. \quad (27)$$

The links of our approach to the method of Skorniakov and Ter-Martirosian [45] are seen from the fact that Eq. (27) leads to the same equation for the Fourier transform of the function  $f(\mathbf{r})$  as in Ref. [45].

We first demonstrate a general approach for solving Eq. (27) and finding the scattering amplitude. For  $r \gg a$ , the second term on the right-hand side of Eq. (23) is exponentially small and can be omitted. Performing the integration in the first term, we reduce Eq. (23) to the form

$$\hat{L}_E f(\mathbf{r}) = \int d^3 q \{ \sqrt{-E + q^2} - \sqrt{-E} \} f(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}), \quad r \gg a, \quad (28)$$

where  $f(\mathbf{q})$  is the Fourier transform of the function  $f(\mathbf{r})$ . Acting twice with the operator  $(\hat{L}_E + \sqrt{-E})$  on the function  $f(\mathbf{r})$  and using Eq. (27), we then obtain

$$(\hat{L}_E + \sqrt{-E})^2 f(\mathbf{r}) = \int d^3 q (q^2 - E) f(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}} = \frac{f(\mathbf{r})}{a^2}. \quad (29)$$

The total energy is given by

$$E = -1/a^2 + k^2, \quad (30)$$

and Eq. (29) immediately transforms into the equation for the free relative atom-dimer motion,

$$(-\nabla_{\mathbf{r}}^2 - k^2)f(\mathbf{r}) = 0, \quad r \gg a. \quad (31)$$

The expansion of the function  $f(\mathbf{r})$  and the amplitude  $F(k, \theta)$  in Legendre polynomials reads (see the Appendix)

$$f(\mathbf{r}) = \sum_{l=0}^{\infty} i^l (2l+1) P_l(\cos \theta) f_l(r), \quad (32)$$

$$F(k, \theta) = \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) F_l(k). \quad (33)$$

For the function  $f_l(r)$ , which describes the scattering with orbital angular momentum  $l$ , the superposition of incident



and scattered waves satisfying Eq. (31) can be written as

$$\sqrt{a/8\pi}f_l(r) = \sqrt{\pi/2kr}\{J_{l+1/2}(kr) + i(2k/\sqrt{3})F_l(k)H_{l+1/2}(kr)\},$$

$$r \gg a, \quad (34)$$

where  $H_{l+1/2}$  is a Hankel function representing an outgoing wave, and  $J_{l+1/2}$  is a Bessel function. For  $kr \rightarrow \infty$ , the Hankel function is  $H_{l+1/2} \approx (-i)^{l+1} \sqrt{2/kr} \exp(ikr)$ . Then, multiplying both sides of Eq. (34) by  $i^l(2l+1)P_l(\cos \theta)$ , making a summation over  $l$ , and taking into account Eqs. (32), (33), and (26), we arrive at Eq. (25).

Using Eq. (32), one reduces Eq. (27) to a set of uncoupled integral equations for the functions  $f_l(r)$ ,

$$(\hat{L}_E^l - a^{-1} + \sqrt{-E})f_l(r) = 0, \quad l = 0, 1, 2, \dots, \quad (35)$$

where the integral operator  $\hat{L}_E^l$  for a given  $l$  is obtained by integrating  $\hat{L}_E$  over  $dO_r/4\pi$  with the weight  $P_l(\cos \theta)$ . Partial scattering amplitudes  $F_l(k)$  are then found by solving Eq. (35) and fitting the obtained  $f_l(r)$  with the asymptotic expression (34). Then, Eqs. (32) and (33) give the function  $f(\mathbf{r})$  and the total scattering amplitude  $F(k, \theta)$ .

In the ultracold limit, where the condition

$$ka \ll 1 \quad (36)$$

is satisfied, the scattering is dominated by the  $s$ -wave contribution and can be analyzed setting  $k=0$  and writing the total energy as  $E=-1/a^2$ . This is clearly seen from Eq. (34) with  $l=0$ , which for  $k \rightarrow 0$  reads

$$f_0(r) \approx \sqrt{8\pi/a}(1 - 2a_{ad}/\sqrt{3}r), \quad r \gg a, \quad (37)$$

where  $a_{ad} = -F_0(0)$  is the atom-dimer scattering length.

Thus, for finding  $a_{ad}$  one should solve Eq. (35) with  $l=0$ , assuming the limit  $k \rightarrow 0$ . This equation then reduces to

$$\hat{L}_E^0 f_0(r) = 0. \quad (38)$$

Using Eq. (15) and integrating over  $dO_r/4\pi$  in Eq. (23), we represent Eq. (38) in the form

$$\hat{L}_E^0 f_0(r) = \frac{1}{\pi ar} \int_0^\infty \left[ [f_0(r) - f_0(r')] \left\{ \frac{K_1(|r' - r|/a)}{|r' - r|} - \frac{K_1[(r + r')/a]}{r + r'} \right\} + 2f_0(r') \left\{ \frac{K_1(\sqrt{r^2 + r'^2 - rr'}/a)}{\sqrt{r^2 + r'^2 - rr'}} - \frac{K_1(\sqrt{r^2 + r'^2 + rr'}/a)}{\sqrt{r^2 + r'^2 + rr'}} \right\} \right] r' dr' = 0, \quad (39)$$

where  $K_1$  is an exponentially decaying Bessel function. It is easily seen that the principal value of the integral in the first line of Eq. (39) is finite. For  $r' \rightarrow r$ , the integrand behaves as  $1/(r - r')$ .

We numerically solved Eq. (39) and found the function  $f_0(r)$  at all distances  $r$ . Fitting the obtained  $f_0(r)$  at  $r \gg a$  with the asymptotic expression (37), we arrived at the atom-dimer scattering length  $a_{ad} = 1.2a$ , which reproduces the result of Ref. [45]. Our calculations also show that the behavior of  $f_0$  suggests a soft-core atom-dimer repulsion, with a range of the order of  $a$ .

## V. RELAXATION IN ATOM-DIMER COLLISIONS

Weakly bound dimers that we are considering are diatomic molecules in the highest rovibrational state. Hence, they can undergo relaxation into deep bound states in their collisions with each other or with unbound atoms. The released binding energy of a deep state is  $\sim \hbar^2/mR_e^2$ . It is transformed into the kinetic energy of particles in the outgoing collisional channel and they escape from the trapped sample. Therefore, the process of collisional relaxation of weakly bound dimers determines the lifetime of a gas of these molecules and, in particular, possibilities to Bose-condense such a gas.

In our previous work [39] we have shown that this process is suppressed due to Fermi statistics for the atoms in combination with a large size of the dimer. The binding energy of the dimers is  $\varepsilon_0 = \hbar^2/ma^2$  and their size is  $\sim a \gg R_e$ . The size of deep bound states is of the order of  $R_e$ . Hence, the relaxation requires the presence of at least three fermions at distances  $\sim R_e$  from each other. As two of them are necessarily identical, due to the Pauli exclusion principle the relaxation probability acquires a small factor proportional to a power of  $(qR_e)$ , where  $q \sim 1/a$  is a characteristic momentum of the atoms in the weakly bound molecular state.

In this section, we discuss relaxation of weakly bound dimers into deep bound states in ultracold atom-dimer collisions satisfying the condition (36). Relying on the inequality  $a \gg R_e$ , we develop a method that allows us to establish a dependence of the relaxation rate on the scattering length  $a$ , without going into a detailed analysis of the short-range behavior of the system of three atoms. It is assumed that the amplitude of the inelastic process of relaxation is much smaller than the amplitude of elastic scattering. Then the dependence of the relaxation rate on  $a$  is related only to the  $a$ -dependence of the initial-state three-body wave function  $\Psi$ .

The relaxation occurs when all of the three atoms approach each other to distances of the order of  $R_e$ . At these interatomic distances, as well as at all distances  $x, y \ll a$ , the wave function  $\Psi$  in the ultracold limit is determined by the Schrödinger equation (11) with  $E=0$ . Therefore, it depends on the scattering length  $a$  only through a normalization coefficient,

$$\Psi = A(a)\psi, \quad x, y \ll a, \quad (40)$$

where the function  $\psi$  is independent of  $a$ . The probability of relaxation and, hence, the relaxation rate constant  $\alpha_{ad}$  are proportional to  $|\Psi|^2$  at distances  $x, y \sim R_e$ . We thus have

$$\alpha_{ad} \propto |A(a)|^2. \quad (41)$$

The goal then is to find the coefficient  $A(a)$ , which determines the dependence of the relaxation rate on  $a$ .

In the region where  $R_e \ll \{x, y\} \ll a$ , the  $a$ -independent function  $\psi$  can be found in the zero-range approximation. Then, matching the wave function  $\Psi$  given by Eq. (40) with the result of the zero-range approximation at interparticle distances larger than  $a$  gives the coefficient  $A(a)$ .

We start with analyzing the behavior of the three-body wave function in the zero-range approximation at distances  $x, y \ll a$ . In this region of distances,  $\Psi$  is reconstructed through the function  $f(\mathbf{r})$  from Eq. (17) with  $h(\mathbf{r})=f(\mathbf{r})$  and  $\Psi_0=0$ , setting  $E \rightarrow 0$ . Accordingly, one should use the Green function  $G_0$  (16) in this equation, which then reads

$$\Psi(\mathbf{x}, \mathbf{y}) = \int \left\{ G_0 \left[ \sqrt{(\mathbf{x} - \mathbf{r}'/2)^2 + (\mathbf{y} + \sqrt{3}\mathbf{r}'/2)^2} \right] - \int G_0 \left[ \sqrt{(\mathbf{x} - \mathbf{r}'/2)^2 + (\mathbf{y} - \sqrt{3}\mathbf{r}'/2)^2} \right] \right\} \times f(\mathbf{r}') d^3 r', \quad x, y \ll a. \quad (42)$$

The main contribution to the integral in Eq. (42) comes from distances  $r' \ll a$  and, hence, we have to find the function  $f$  at these distances. In the ultracold limit where the condition (36) is satisfied, the inelastic process of relaxation is dominated by the contribution of the  $s$ -wave channel. As we found in Sec. IV, the  $s$ -wave part  $f_0$  of the function  $f$  is determined by Eqs. (38) and (39). For  $r \ll a$ , the distances  $r'$  in Eq. (39) are also much smaller than  $a$ . This is equivalent to setting the limit  $E \rightarrow 0$  ( $a^{-1} \rightarrow 0$ ) for the integral operator  $\hat{L}_E^0$  in Eq. (39), and this operator then reduces to

$$\hat{L}_0^0 f_0(r) = \frac{1}{\pi r} \int_0^\infty \left[ [f_0(r) - f_0(r')] \left\{ \frac{1}{(r' - r)^2} - \frac{1}{(r + r')^2} \right\} + 2f_0(r') \left\{ \frac{1}{r^2 + r'^2 - rr'} - \frac{1}{r^2 + r'^2 + rr'} \right\} \right] r' dr', \quad (43)$$

where the integration of the term containing  $(r - r')^2$  assumes a principal value of the integral.

Thus, the function  $f_0(r)$  at  $r \ll a$  is a solution of the integral equation

$$\hat{L}_0^0 f_0(r) = 0. \quad (44)$$

The operator  $\hat{L}_0^0$  has a property that  $\hat{L}_0^0 r^\nu = \lambda(\nu) r^{\nu-1}$  for  $-5 < \text{Re}(\nu) < 3$ , and the integral in Eq. (43) diverges outside this interval. The function  $\lambda(\nu)$  is given by

$$\lambda(\nu) = (\nu + 1) \tan \frac{\pi \nu}{2} + \frac{4}{\sqrt{3}} \frac{\sin[\pi(\nu + 1)/6]}{\cos(\pi \nu/2)}. \quad (45)$$

In the specified interval of  $\nu$  the function  $\lambda$  has two roots,  $\nu_+ = 1.166$  and  $\nu_- = -3.166$ . Accordingly, the solution of Eq. (44) is a linear superposition,

$$f_0(r) \approx C_+ r^{\nu_+} + C_- r^{\nu_-}, \quad r \ll a. \quad (46)$$

The determination of the ratio  $C_+/C_-$  involves short-range physics and is beyond the scope of this paper. However, in the absence of a three-body resonance, the matching procedure implies that at distances  $r \sim R_e$  both terms in Eq. (46) are of the same order of magnitude. So  $C_+/C_- \propto R_e^{-4.332}$ , and at distances  $r \gg R_e$  one has  $f_0(r) \approx C_+ r^{\nu_+}$ . Substituting this result into Eq. (42), we find that at distances  $x, y \ll a$  the three-body wave function takes the form

$$\Psi \approx \Phi^0(\Omega) f(\rho) / \rho = C_+ \Phi^0(\Omega) \rho^{\nu_+ - 1}, \quad x, y \ll a, \quad (47)$$

where  $\rho = \sqrt{x^2 + y^2}$  is the hyperradius, and the set of hyperangles  $\Omega$  denotes all the other coordinates. Although one can explicitly write down the function  $\Phi^0(\Omega)$ , for us it is only important that this function is  $a$ -independent.

Comparing Eq. (47) with Eq. (40), we see that one may set  $\psi = \Phi^0(\Omega) \rho^{\nu_+ - 1}$  in the interval of distances where  $R_e \ll \{x, y\} \ll a$ . We then have  $C_+ = A(a)$ , i.e., the function  $f_0$  can be written as

$$f_0(r) \approx A(a) r^{\nu_+}, \quad r \ll a. \quad (48)$$

Numerical integration of Eq. (39) shows that  $f_0$  smoothly interpolates between the asymptotic expressions given by Eq. (48) for  $r \ll a$ , and by Eq. (37) for  $r \gg a$ . This procedure provides matching of the two asymptotes at  $r \sim a$  and gives the coefficient

$$A(a) \propto a^{-1/2 - \nu_+}. \quad (49)$$

In fact, the result of Eq. (49) can be obtained in a more elegant way, using only Eqs. (37) and (48). In the zero-range approximation, the only distance scale is the two-body scattering length  $a$ . Hence, we may rescale the coordinate and represent the function  $f_0$  in the form

$$f_0(r) = B(a) \tilde{f}_0(r/a), \quad (50)$$

where  $\tilde{f}_0$  depends on  $a$  only through the rescaled coordinate  $r/a$ . The coefficient  $B(a)$  is independent of the coordinate and can be obtained by comparing Eq. (50) with asymptotic expressions (37) and (48). Using Eq. (37), we see that  $B \propto a^{-1/2}$ , whereas the comparison of Eq. (50) with Eq. (48) gives  $B \propto A(a) a^{\nu_+}$ . This immediately leads to Eq. (49) for the coefficient  $A(a)$ .

As the dependence of the relaxation rate constant  $\alpha_{ad}$  on the two-body scattering length is governed by Eq. (41), using Eq. (49) we obtain  $\alpha_{ad} \propto a^{-s}$ , where  $s = 1 + 2\nu_+ \approx 3.33$ . The absolute value of the relaxation rate is determined by the contribution of interparticle distances  $\sim R_e$ , where the zero-range approximation is not valid. This approximation only gives a correct dependence of the relaxation rate on  $a$ .

Assuming that the short-range physics is characterized by the length scale  $R_e$  and by the energy scale  $\hbar^2/mR_e^2$ , we can restore the dimensions and write the following expression for the rate constant of relaxation of weakly bound dimers into deep bound states in atom-dimer ultracold collisions:

$$\alpha_{ad} = C(\hbar R_e/m)(R_e/a)^s, \quad s = 3.33. \quad (51)$$

One clearly sees that the relaxation rate rapidly decreases with increasing the two-body scattering length. However, the coefficient  $C$  depends on a particular system.

The relaxation due to atom-dimer scattering with nonzero orbital angular momenta is very small. Since the atom-dimer effective interaction has a characteristic range  $\sim a$  (see Sec. IV), the  $p$ -wave part of the three-body wave function  $\Psi$  at short interparticle distances is proportional to  $ka$ . Hence, the  $p$ -wave contribution to the relaxation rate is  $\propto (ka)^2$  and can be omitted for ultracold collisions satisfying the condition (36).

## VI. ELASTIC DIMER-DIMER SCATTERING

As we already mentioned in the Introduction, elastic interaction between weakly bound bosonic molecules of  $\uparrow$  and  $\downarrow$  fermionic atoms is important for understanding the physics of their Bose-Einstein condensation and for studying the BCS-BEC crossover in two-component atomic Fermi gases. The dimer-dimer elastic scattering is a four-body problem described by the Schrödinger equation,

$$\left\{ \begin{aligned} & -\nabla_{\mathbf{r}_1}^2 - \nabla_{\mathbf{r}_2}^2 - \nabla_{\mathbf{R}}^2 + U(r_1) + U(r_2) + \sum_{\pm} U[(\mathbf{r}_1 + \mathbf{r}_2 \pm \sqrt{2}\mathbf{R})/2] \\ & - E \end{aligned} \right\} \Psi = 0. \quad (52)$$

Here we again use units in which  $\hbar = m = 1$ . The distance between two given  $\uparrow$  and  $\downarrow$  fermions is  $\mathbf{r}_1$ , and  $\mathbf{r}_2$  is the distance between the other two. The distance between the centers of mass of these pairs is  $\mathbf{R}/\sqrt{2}$ , and  $(\mathbf{r}_1 + \mathbf{r}_2 \pm \sqrt{2}\mathbf{R})/2$  are the separations between  $\uparrow$  and  $\downarrow$  fermions in the other two possible  $\uparrow\downarrow$  pairs. The total energy is  $E = -2\varepsilon_0 + \varepsilon$ , with  $\varepsilon$  being the collision energy and  $\varepsilon_0 = -1/a^2$  the binding energy of a dimer.

The wave function  $\Psi$  is symmetric with respect to the permutation of bosonic  $\uparrow\downarrow$  pairs and antisymmetric with respect to permutations of identical fermions,

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) &= \Psi(\mathbf{r}_2, \mathbf{r}_1, -\mathbf{R}) \\ &= -\Psi\left(\frac{\mathbf{r}_1 + \mathbf{r}_2 \pm \sqrt{2}\mathbf{R}}{2}, \frac{\mathbf{r}_1 + \mathbf{r}_2 \mp \sqrt{2}\mathbf{R}}{2}, \pm \frac{\mathbf{r}_1 - \mathbf{r}_2}{\sqrt{2}}\right). \end{aligned} \quad (53)$$

The weak binding of atoms in the dimer assumes that the two-body (positive) scattering length is  $a \gg R_e$ , and we employ the zero-range approximation in our analysis of the molecule-molecule scattering. This is done relying on the formulation of this approximation given in Sec. III for the three-body problem. Thus, the four-body system is described by the free-particle Schrödinger equation

$$-[\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2 + \nabla_{\mathbf{R}}^2 + E]\Psi = 0, \quad (54)$$

and the four-body wave function  $\Psi$  should satisfy the Bethe-Peierls boundary condition for a vanishing distance in any pair of  $\uparrow$  and  $\downarrow$  fermions, i.e., for  $\mathbf{r}_1 \rightarrow \mathbf{0}$ ,  $\mathbf{r}_2 \rightarrow \mathbf{0}$ , and  $\mathbf{r}_1 + \mathbf{r}_2 \pm \sqrt{2}\mathbf{R} \rightarrow \mathbf{0}$ . Due to the symmetry, it is necessary to require a proper behavior of  $\Psi$  only at one of these boundaries. For  $\mathbf{r}_1 \rightarrow \mathbf{0}$ , the boundary condition reads

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) \rightarrow f(\mathbf{r}_2, \mathbf{R})(1/4\pi r_1 - 1/4\pi a). \quad (55)$$

The function  $f(\mathbf{r}_2, \mathbf{R})$  is analogous to that defined in Sec. III and it contains the information about the second pair of particles when the first two are sitting on top of each other.

In the ultracold limit, where the condition (36) is satisfied, the scattering is dominated by the contribution of the  $s$ -wave channel. The inequality (36) is equivalent to  $\varepsilon \ll \varepsilon_0$  and, hence, the  $s$ -wave scattering can be analyzed from the solution of Eq. (54) with  $E = -2\varepsilon_0 < 0$ . For large  $R$ , the corresponding wave function is given by

$$\Psi \approx \phi_0(r_1)\phi_0(r_2)(1 - \sqrt{2}a_{dd}/R), \quad R \gg a, \quad (56)$$

where  $a_{dd}$  is the dimer-dimer scattering length, and the wave function of the weakly bound dimer is given by Eq. (10). Combining Eqs. (55) and (56), we obtain the asymptotic expression for  $f$  at large distances  $R$ ,

$$f(\mathbf{r}_2, \mathbf{R}) \approx (2/r_2 a) \exp(-r_2/a) (1 - \sqrt{2}a_{dd}/R), \quad R \gg a. \quad (57)$$

In the case of the  $s$ -wave scattering, the function  $f$  depends only on three variables: the absolute values of  $\mathbf{r}_2$  and  $\mathbf{R}$ , and the angle between them. We now derive and solve the equation for  $f$ . The value of  $a_{dd}$  is then deduced from the behavior of  $f$  at large  $R$  governed by Eq. (57).

We first establish a general form of the wave function  $\Psi$  satisfying Eq. (54), with the boundary condition (55) and symmetry relations (53). In our case, the total energy  $E = -2/a^2 < 0$ , and the Green function of Eq. (54) reads

$$G(X) = (2\pi)^{-9/2} (Xa/\sqrt{2})^{-7/2} K_{7/2}(\sqrt{2}X/a), \quad (58)$$

where  $X = |S - S'|$ , and  $S = \{\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}\}$  is a nine-component vector. Accordingly, one has  $|S - S'| = \sqrt{(\mathbf{r}_1 - \mathbf{r}'_1)^2 + (\mathbf{r}_2 - \mathbf{r}'_2)^2 + (\mathbf{R} - \mathbf{R}')^2}$ . In analogy with the three-body case, the four-body wave function  $\Psi$  can be expressed through  $G(|S - S'|)$  with coordinates  $S'$  corresponding to a vanishing distance between  $\uparrow$  and  $\downarrow$  fermions, i.e., for  $\mathbf{r}'_1 \rightarrow \mathbf{0}$ ,  $\mathbf{r}'_2 \rightarrow \mathbf{0}$ , and  $(\mathbf{r}'_1 + \mathbf{r}'_2 \pm \sqrt{2}\mathbf{R}')/2 \rightarrow \mathbf{0}$ . Thus, for the wave function satisfying the symmetry relations (53), we have

$$\begin{aligned} \Psi(S) &= \Psi_0 + \int d^3r' d^3R' [G(|S - S_1|) + G(|S - S_2|) \\ &\quad - G(|S - S_+|) - G(|S - S_-|)] h(\mathbf{r}', \mathbf{R}'), \end{aligned} \quad (59)$$

where  $S_1 = \{0, \mathbf{r}', \mathbf{R}'\}$ ,  $S_2 = \{\mathbf{r}', 0, -\mathbf{R}'\}$ , and  $S_{\pm} = \{\mathbf{r}'/2 \pm \mathbf{R}'/\sqrt{2}, \mathbf{r}'/2 \mp \mathbf{R}'/\sqrt{2}, \mp \mathbf{r}'\sqrt{2}\}$ . The function  $\Psi_0$  is a properly symmetrized finite solution of Eq. (54), regular at vanishing distances between  $\uparrow$  and  $\downarrow$  fermions. For  $E < 0$ , nontrivial solutions of this type do not exist and we have to put  $\Psi_0 = 0$ . The function  $h(\mathbf{r}_2, \mathbf{R})$  has to be determined by comparing  $\Psi$  (59) at  $\mathbf{r}_1 \rightarrow \mathbf{0}$ , with the boundary condition (55).

This procedure is similar to that developed in Sec. III for the three-body case. Considering the limit  $\mathbf{r}_1 \rightarrow \mathbf{0}$ , we extract the leading terms on the right-hand side of Eq. (59). These are the terms that behave as  $1/r_1$  or remain finite in this limit. The last three terms in the square brackets in Eq. (59) provide a finite contribution

$$\begin{aligned} & \int d^3r' d^3R' h(\mathbf{r}', \mathbf{R}') [G(|\bar{S}_2 - S_2|) \\ & \quad - G(|\bar{S}_2 - S_+|) - G(|\bar{S}_2 - S_-|)], \end{aligned} \quad (60)$$

where  $\bar{S}_2 = \{0, \mathbf{r}_2, \mathbf{R}\}$ . For finding the contribution of the first term in the square brackets, we subtract from this term and add to it an auxiliary quantity,

$$h(\mathbf{r}_2, \mathbf{R}) \int G(|S - S_1|) d^3 r' d^3 R' = \frac{h(\mathbf{r}_2, \mathbf{R})}{4\pi r_1} \exp(-\sqrt{2}r_1/a). \quad (61)$$

The result of the subtraction yields a finite contribution which for  $r_1 \rightarrow 0$  can be written as

$$\begin{aligned} & \int d^3 r' d^3 R' [h(\mathbf{r}', \mathbf{R}') - h(\mathbf{r}_2, \mathbf{R})] G(|S - S_1|) \\ &= P \int d^3 r' d^3 R' [h(\mathbf{r}', \mathbf{R}') - h(\mathbf{r}_2, \mathbf{R})] G(|\bar{S}_2 - S_1|), \end{aligned} \quad (62)$$

with the symbol P standing for the principal value of the integral over  $dr'$  (or  $dR'$ ). Equation (62) is derived in the Appendix and it is proven that the integral in the second line of this equation is convergent.

In the limit  $r_1 \rightarrow 0$ , the right-hand side of Eq. (61) is equal to

$$h(\mathbf{r}_2, \mathbf{R}) (1/4\pi r_1 - \sqrt{2}/4\pi a). \quad (63)$$

We thus find that for  $\mathbf{r}_1 \rightarrow \mathbf{0}$ , the wave function  $\Psi$  of Eq. (59) takes the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = \frac{h(\mathbf{r}_2, \mathbf{R})}{4\pi r_1} + \mathcal{R}, \quad \mathbf{r}_1 \rightarrow \mathbf{0}, \quad (64)$$

where  $\mathcal{R}$  is the sum of regular  $r_1$ -independent terms given by Eqs. (60) and (62), and by the second term on the right-hand side of Eq. (63). Equation (64) should coincide with Eq. (55), and comparing the singular terms of these equations we find  $h(\mathbf{r}_2, \mathbf{R}) = f(\mathbf{r}_2, \mathbf{R})$ . As the quantity  $\mathcal{R}$  should coincide with the regular term of Eq. (55), equal to  $-f(\mathbf{r}_2, \mathbf{R})/4\pi a$ , we obtain the following equation for the function  $f$ :

$$\begin{aligned} & \int d^3 r' d^3 R' \left\{ G(|\bar{S} - S_1|) [f(\mathbf{r}', \mathbf{R}') - f(\mathbf{r}, \mathbf{R})] + [G(|\bar{S} - S_2|) \right. \\ & \left. - \sum_{\pm} G(|\bar{S} - S_{\pm}|)] f(\mathbf{r}', \mathbf{R}') \right\} = (\sqrt{2} - 1) f(\mathbf{r}, \mathbf{R}) / 4\pi a. \end{aligned} \quad (65)$$

Here  $\bar{S} = \{0, \mathbf{r}, \mathbf{R}\}$ , and we omitted the symbol of principal value for the integral in the first line of Eq. (65).

As we already mentioned above, for the  $s$ -wave scattering the function  $f(\mathbf{r}, \mathbf{R})$  depends only on the absolute values of  $\mathbf{r}$  and  $\mathbf{R}$  and on the angle between them. Thus, Eq. (65) is an integral equation for the function of three variables. We have solved this equation numerically for all distances  $R$  and  $r$ , and all angles between the vectors  $\mathbf{R}$  and  $\mathbf{r}$ . Fitting the asymptotic expression (57) at  $R \gg a$  with the function  $f(\mathbf{r}, \mathbf{R})$  obtained numerically from Eq. (65), we find with 2% accuracy that the dimer-dimer scattering length is

$$a_{dd} = 0.6a > 0. \quad (66)$$

Our calculations show the absence of four-body weakly bound states, and the behavior of  $f$  at small  $R$  suggests a soft-core repulsion between dimers, with a range  $\sim a$ .

The result of Eq. (66) is exact, and its derivation was outlined in our previous work [39]. Equation (66) indicates the stability of molecular BEC with respect to collapse. Compared to earlier studies which assumed  $a_{dd} = 2a$  [4], Eq. (66) gives almost twice as small a sound velocity of the molecular condensate and a rate of elastic collisions smaller by an order of magnitude. We should mention here that the result of earlier studies [4] was reconsidered in Ref. [48] by using a diagrammatic approach which leads to  $a_{dd} = 0.75a$ . However, this approach misses a number of diagrams which give a contribution of the same order of magnitude as those taken into account.

## VII. RELAXATION IN DIMER-DIMER COLLISIONS

In this section, we generalize the results obtained in Sec. V to the relaxation of weakly bound dimers into deep bound states in dimer-dimer collisions. We again consider the ultracold limit described by the condition (36), where the relaxation process is dominated by the contribution of the  $s$ -wave dimer-dimer scattering. The key point of our discussion is that the dimer-dimer relaxation collisions are to a large extent similar to the atom-dimer ones.

Indeed, the relaxation process requires only three atoms to approach each other to short distances of the order of  $R_e$ . The fourth particle can be at a large distance from these three and, in this respect, does not participate in the relaxation process. This distance is of the order of the size of a dimer, which is  $\sim a \gg R_e$ . As well as in the case of atom-dimer collisions, the dependence of the relaxation rate on the two-body scattering length  $a$  is determined by the  $a$ -dependence of the initial-state wave function  $\Psi$ . We thus see that the configuration space contributing to the relaxation probability can be viewed as a system of three atoms at short distances  $\sim R_e$  from each other and a fourth atom separated from this system by a large distance  $\sim a$ . In this case, the four-body wave function decomposes into a product,

$$\Psi = \eta(\mathbf{z}) \Psi^{(3)}(\rho, \Omega), \quad (67)$$

where  $\Psi^{(3)}$  is the wave function of the three-fermion system,  $\rho$  and  $\Omega$  are the hyperradius and the set of hyperangles for these fermions,  $\mathbf{z}$  is the distance between their center of mass and the fourth atom, and the function  $\eta(\mathbf{z})$  describes the motion of this atom. Note that Eq. (67) remains valid for any hyperradius  $\rho \ll |\mathbf{z}| \sim a$ .

The transition to a deep bound two-body state occurs in the system of three atoms and does not change the wave function of the fourth atom,  $\eta(\mathbf{z})$ . Therefore, averaging the transition probability over the motion of the fourth particle, the rate constant of relaxation in dimer-dimer collisions can be written as

$$\alpha_{dd} = \alpha^{(3)} \int |\eta(\mathbf{z})|^2 d^3 z = \alpha^{(3)}, \quad (68)$$

where  $\alpha^{(3)}$  is the rate constant of relaxation for the three-atom system.

We thus obtain that the problem is reduced to the relaxation in atom-dimer collisions. The difference from the case



discussed in Sec. V is that now the relative momentum of the collision is  $\sim 1/a$ . This is seen by considering  $\Psi^{(3)}$  at large distances between the dimer and the fermionic atom, hereafter referred to as the third fermion. This fermion is in the bound molecular state with the fourth atom. As the size of this state is  $\sim a$ , the expansion of the wave function of the third fermion in plane waves shows that its momentum  $q$  is of the order of  $1/a$ .

Keeping in mind the discussion in Sec. V, we see that the result for the relaxation rate following from Eq. (51) remains valid for the dimer-dimer collisions. The fact that the relative momentum is  $q \sim 1/a$  can only change the numerical coefficient, not the dependence of the relaxation rate constant on the two-body scattering length  $a$ . However, the result of Eq. (51) accounts only for the  $s$ -wave scattering of the third fermionic atom on the dimer, which provides the leading relaxation channel for ultracold atom-dimer collisions. In the case of dimer-dimer collisions, there is a relaxation channel that is more important in the limit of large  $a$  (see below). For the  $s$ -wave dimer-dimer scattering, both the fourth and the third fermions (bound to each other in the molecular state) can undergo the  $p$ -wave scattering on the other dimer in such a way that their total orbital angular momentum is equal to zero. We thus should consider the relaxation for the  $p$ -wave collisions between the third fermionic atom and the dimer. These collisions are not suppressed as their relative momentum is  $q \sim 1/a$ .

As we discussed in Sec. V, for the hyperradius  $\rho \ll a$  the wave function of the three-fermion system,  $\Psi^{(3)}$ , depends on the scattering length  $a$  only through a normalization coefficient and can be written in the form (40). We thus have  $\Psi^{(3)} = A(a)\psi$ , with  $a$ -independent function  $\psi$ , and the relaxation rate constant depends on  $a$  as  $\alpha_{dd} \propto |A(a)|^2$ . This requires us to find the coefficient  $A(a)$  for the case of the  $p$ -wave scattering of the third fermionic atom on the molecule. We will do this in the zero-range approximation, along the lines of our discussion of the  $s$ -wave atom-dimer scattering in Sec. V.

We first consider the region of interparticle distances where  $R_e \ll \rho \ll a$ . Then the function  $f(\mathbf{r})$  for the three-body problem is determined by Eq. (27) in which we have to set the limit  $E \rightarrow 0$  and  $a^{-1} \rightarrow 0$ . Therefore, the integral equation (35) for the  $p$ -component of the function  $f$  takes the form

$$\hat{L}_0^1 f_1(r) = 0, \quad (69)$$

where the operator  $\hat{L}_0^1$  is obtained substituting the expansion (32) into Eq. (23) with the Green function  $G_0$  (16), multiplying by  $\cos \theta$ , and integrating over the angles. This yields

$$\begin{aligned} \hat{L}_0^1 f_1(r) = & \frac{1}{\pi} \int_0^\infty dr' \left( \frac{r'}{r} \left[ f_1(r) - f_1(r') \right] \left\{ \frac{1}{(r' - r)^2} \right. \right. \\ & \left. \left. - \frac{1}{(r + r')^2} \right\} + 2f_1(r') \left\{ \frac{1}{r^2 + r'^2 - rr'} \right. \right. \\ & \left. \left. + \frac{1}{r^2 + r'^2 + rr'} - \frac{1}{(r + r')^2} \right\} \right) + \frac{2f_1(r')}{r^2} \end{aligned}$$

$$\times \ln \frac{\sqrt{(r+r')(r^2+r'^2-rr')}}{\sqrt{|r-r'|(r^2+r'^2+rr')}}), \quad (70)$$

where one should take a principal value for the integral of the term containing  $(r-r')^2$ .

Like the operator  $L_0^0$ , the operator  $L_0^1$  has a property  $\hat{L}_0^1 r^\nu = \lambda(\nu)r^{\nu-1}$  for  $-4 < \text{Re}(\nu) < 2$ . The function  $\lambda(\nu)$  is now given by

$$\lambda(\nu) = \frac{4}{\sqrt{3}} \frac{\nu \cos[\pi(\nu+1)/6] - 2 \sin(\pi\nu/6)}{(\nu+1)\sin(\pi\nu/2)} + \frac{\nu(\nu+2)}{\nu+1} \cot \frac{\pi\nu}{2} \quad (71)$$

and has two roots:  $\nu_+ = 0.773$  and  $\nu_- = -2.773$ . Then, with the same arguments as in between Eqs. (45) and (48) in Sec. V, we obtain short-distance expressions for the function  $f_1$  and for the part of the three-body wave function  $\Psi^{(3)}$  corresponding to the  $p$ -wave scattering of the third fermion on the molecule,

$$f_1(r) \approx A(a)a^{\nu_+}(r/a)^{\nu_+}, \quad r \ll a; \quad (72)$$

$$\Psi^{(3)} = A(a)\Phi^1(\Omega)\rho^{\nu_+-1}, \quad \rho \ll a, \quad (73)$$

where the function  $\Phi^1$  is independent of  $a$ .

For relative momenta  $k \sim 1/a$ , the two-body scattering length remains the only distance scale of the zero-range approximation. In particular, the  $p$ -wave scattering amplitude in Eq. (34) will be  $F_1 \sim a$ . We therefore can write the function  $f_1$  in the form (50):  $f_1(r) = B(a)\tilde{f}_1(r/a)$ , where  $\tilde{f}_1$  depends on  $a$  only through the rescaled coordinate  $r/a$ . In order to be consistent with Eq. (34) for  $k \sim 1/a$ , we have to put  $B(a) \propto a^{-1/2}$ . Then the comparison of the resulting  $f_1$  with Eq. (72) gives the coefficient  $A(a) \propto a^{-1/2-\nu_+}$  and the relaxation rate constant is  $\alpha_{dd} \propto |A(a)|^2 \propto a^{-s}$ , with  $s = 1 + 2\nu_+ \approx 2.55$ . Restoring the dimensions, we have

$$\alpha_{dd} = C(\hbar R_e/m)(R_e/a)^s, \quad s = 2.55. \quad (74)$$

One can think of the relaxation mechanism, where the scattering of the third fermion on the dimer occurs with higher orbital angular momenta  $l$ . In this case, the fourth atom scatters on the dimer with the same  $l$ , and the total angular momentum of the dimer-dimer scattering should be equal to zero. Our analysis shows that these scattering mechanisms lead to a power-law dependence  $\alpha_{dd} \propto a^{-s}$ , with larger values of  $s$  than in Eq. (74). Hence, for large  $a$  they can be neglected.

Equation (74) shows a slower decrease of the relaxation rate with increasing  $a$  than in the case of atom-dimer collisions. Obviously, in the limit  $R_e/a \rightarrow 0$  the dimer-dimer relaxation should dominate over the atom-dimer one. The competition between these two relaxation processes can be present if the ratio  $R_e/a$  is not too small and the densities of dimers and atoms in the gas are comparable with each other.

## VIII. WIDE AND NARROW FESHBACH RESONANCES

In experiments with alkali-metal atom gases, large values of the two-body scattering length are achieved by using

Feshbach resonances. In the vicinity of the resonance, the two-body problem is characterized by a strong coupling between the continuum states of colliding atoms and a bound molecular state of another hyperfine domain of these atoms. The resulting scattering length depends on the detuning from the resonance, i.e., on the energy difference  $\Delta$  between the border of the continuum of colliding atoms and the bound molecular state. The splitting between the two hyperfine domains and, hence, the detuning  $\Delta$  depend on the magnetic field, which makes the scattering length tunable by varying the field.

One thus has a two-channel problem which can be described in terms of Breit-Wigner scattering [42,49], the open channel being the states of colliding atoms and the closed channel the bound molecular state of the other hyperfine domain. Various aspects of this type of problem have been discussed by Feshbach [50] and Fano [51]. In cold atom physics, the idea of Feshbach resonances was introduced in Ref. [52], and optically induced resonances have been discussed in Refs. [53,54].

We now analyze to which extent our results for three-atom and four-atom systems of fermions with a positive two-body scattering length  $a \gg R_e$  describe the situation of Feshbach resonances. For low collision energies  $\varepsilon$ , omitting the (small) background scattering length, the scattering amplitude is given by [42]

$$F(\varepsilon) = -\frac{\hbar \gamma / \sqrt{m}}{\varepsilon + \Delta + i \gamma \sqrt{\varepsilon}}, \quad (75)$$

where the quantity  $\hbar \gamma / \sqrt{m} \equiv W$  characterizes the coupling between the two hyperfine domains. In Eq. (75), the detuning  $\Delta$  is positive if the bound molecular state is below the continuum of colliding atoms. Then for  $\Delta > 0$  we have a positive scattering length near the resonance,  $a = -F(0) = W/\Delta$ . Introducing a characteristic length

$$R^* = \hbar^2/mW \quad (76)$$

and expressing the scattering amplitude through the relative momentum of particles  $k = \sqrt{m\varepsilon}/\hbar$ , Eq. (75) takes the form

$$F(k) = -\frac{1}{a^{-1} + R^*k^2 + ik}. \quad (77)$$

The validity of Eq. (77) does not require the inequality  $kR^* \ll 1$ . At the same time, Eq. (77) formally coincides with the amplitude of scattering of slow particles by a potential with the same scattering length  $a$  and an effective range  $R = -2R^*$ , valid under the condition  $kR \ll 1$ .

The length  $R^*$  is an intrinsic parameter of the Feshbach resonance problem. It characterizes the width of the resonance. From Eqs. (75) and (76) we see that large  $W$  and, hence, small  $R^*$  correspond to a wide resonance, whereas small  $W$  and large  $R^*$  lead to a narrow resonance. The issue of wide and narrow resonances is now actively being discussed in the literature [17,19,55–59]. We would like to point out here that the use of the terms “wide” and “narrow” depends on the problem under consideration. For example, in the unitarity limit where  $a \rightarrow \pm\infty$ , Eq. (77) shows that the length  $R^*$  drops out of the problem under the condition  $kR^*$

$\ll 1$ . In a quantum degenerate Fermi gas, the characteristic momentum of particles is the Fermi momentum  $k_F = (3\pi^2 n)^{1/3}$ , where  $n$  is the gas density. Thus, the inequality  $k_F R^* \ll 1$ , referred to as the condition of a wide resonance, ensures universality of the problem [19,55,57–59]. The only length and energy scales in the gas will be the mean interparticle separation  $n^{-1/3}$  and the Fermi energy  $E_F = (3\pi^2 n)^{2/3} \hbar^2/2m$ , and the system acquires universal thermodynamics [16].

In our case, the situation is different. We are considering weakly bound diatomic molecules in the open channel with a binding energy (9), and our discussion of atom-dimer and dimer-dimer collisions assumes that there is a weakly interacting gas of these dimers and atoms. The most important limitation is related to the binding energy and the wave function of the dimers. The energy of the weakly bound molecular state is determined by the pole of the scattering amplitude (77). One then finds that this state exists only for  $a > 0$  and the universal expression (9) used in our calculations,  $\varepsilon_0 = \hbar^2/ma^2$ , requires the inequality [56]

$$R^* \ll a. \quad (78)$$

Under this condition, the wave function of the weakly bound molecular state has only a small admixture of the closed channel [56].

Our calculations for the atom-dimer and dimer-dimer collisions were done in the ultracold limit where  $ka \ll 1$ . In a thermal gas of atoms and dimers, the characteristic momentum is the thermal momentum  $k_T = (2mT/\hbar^2)^{1/2}$ , whereas for a degenerate, in particular Bose-condensed gas of the dimers, the characteristic momentum is the inverse healing length,  $(na)^{1/2}$ . In both cases, the inequality  $ka \ll 1$  assumes the weakly interacting regime, where  $na^3 \ll 1$ . One can also see that in the limit  $ka \ll 1$ , the inequality Eq. (78) makes the scattering amplitude  $F(k)$  (77) momentum independent and equal to  $-a$ . This justifies the use of our single-channel zero-range approximation for calculating atom-dimer and dimer-dimer interactions and collisional properties. We thus obtain that for our problem the condition of a wide Feshbach resonance is given by Eq. (78). Under this condition, the problem is universal in the sense that the size of weakly bound dimers, and atom-dimer and dimer-dimer scattering properties, are characterized by a single parameter, the two-body scattering length  $a$ .

Note that the interaction between the two channels of the Feshbach problem is efficient at interparticle distances which are of the order of  $R_e$ . Therefore, the Feshbach character of scattering does not influence the condition  $a \gg R_e$  that allows us to use the zero-range approximation for the entire region of interparticle distances.

## IX. CONCLUDING REMARKS

In most experiments with weakly bound diatomic molecules produced by using Feshbach resonances in a degenerate two-component atomic Fermi gas, the wide resonance condition (78) was satisfied. This was the case with  $^{40}\text{K}_2$  molecules at JILA [28,29,34], and with  $^6\text{Li}_2$  at Innsbruck [26,30,37,38], MIT [31,35], Duke [14,36], ENS [15,25,32],

and Rice [33]. In these experimental studies, the length  $R^*$  is of the order of or smaller than  $20 \text{ \AA}$ , and for the achieved values of the scattering length  $a$  from  $500$  to  $2000 \text{ \AA}$ , the ratio  $R^*/a$  is smaller than  $0.1$ . The only exception is the experiment at Rice with  ${}^6\text{Li}$  near a narrow Feshbach resonance at  $543 \text{ G}$  [27]. For this resonance, the length  $R^*$  is large and at obtained values of  $a$  the condition (78) is not fulfilled. Therefore, the Rice experiment [27] cannot be described by our theory.

Experimental studies of dimers produced in a Fermi gas by using wide Feshbach resonances at JILA, Innsbruck, MIT, and ENS are well described within our theoretical approach. It should be mentioned that for  $a > 0$  and equal concentrations of the two atomic components of the gas, at temperatures well below  $E_F$  practically all atoms should be converted into dimers if the gas density satisfies the inequality  $na^3 \ll 1$  [60]. In ongoing experiments, the imbalance between the atomic components is fairly small, and at sufficiently low temperatures there can only be a small fraction of unpaired fermionic atoms.

The results at JILA [28,29,34], Innsbruck [26,30,37], MIT [31,35], ENS [25,32], and Rice [33] show a remarkable collisional stability of weakly bound diatomic molecules  ${}^{40}\text{K}_2$  and  ${}^6\text{Li}_2$ . At molecular densities  $n \sim 10^{13} \text{ cm}^{-3}$ , the lifetime of the gas ranges from tens of milliseconds to tens of seconds, depending on the value of the scattering length  $a$ . A strong decrease of the relaxation rate with increasing  $a$ , following from Eq. (74), is consistent with experimental data. The potassium experiment at JILA [28] and the lithium experiment at ENS [32] give the relaxation rate constant  $\alpha_{dd} \propto a^{-s}$ , where  $s \approx 2.3$  with 15% accuracy for  $\text{K}_2$ , and  $s \approx 2.0$  with 40% accuracy for  $\text{Li}_2$ . The absolute value of the rate constant for a thermal gas of  $\text{Li}_2$  is  $\alpha_{dd} \approx 2 \times 10^{13} \text{ cm}^3/s$  for the scattering length  $a \approx 800 \text{ \AA}$  [25]. For  $\text{K}_2$  it is by an order of magnitude higher at the same value of  $a$  [28], which can be a consequence of a larger value of the characteristic radius of interaction  $R_e$ .

At realistic temperatures, the relaxation rate constant  $\alpha_{dd}$  is much smaller than the rate constant of elastic collisions  $8\pi a_{dd}^2 v_T$ , where  $v_T$  is the thermal velocity. For example, for the  $\text{Li}_2$  weakly bound dimers at a temperature  $T \sim 3 \text{ \mu K}$  and  $a \sim 800 \text{ \AA}$ , the corresponding ratio is of the order of  $10^{-4}$  or  $10^{-5}$ . This opens wide possibilities for reaching BEC of the dimers and cooling the Bose-condensed gas to temperatures of the order of its chemical potential. Long-lived BEC of weakly bound dimers has been recently observed for  ${}^{40}\text{K}_2$  at JILA [29,34] and for  ${}^6\text{Li}_2$  at Innsbruck [30,37], MIT [31,35], ENS [32], and Rice [33]. Measurements of the dimer-dimer scattering length in these experiments confirm our result  $a_{dd} = 0.6a$  [39] with accuracy up to 30%. This result is also confirmed by recent Monte Carlo calculations [61] of the ground-state energy in the molecular BEC regime (see also [62]).

In conclusion, we have developed a theory of elastic and inelastic collisions of weakly bound molecules formed in a two-component atomic Fermi gas. We emphasize that the remarkable collisional stability of these molecules at  $a \gg R_e$  is due to *Fermi statistics*. This effect is not present for weakly bound molecules of bosonic atoms, even if they have the same large size. Indeed, identical fermionic atoms par-

ticipating in the relaxation process at short interparticle distances have very small relative momenta  $k \sim 1/a$  and, hence, the process is suppressed compared to the case of molecules of bosonic atoms.

The long lifetime of weakly bound diatomic molecules of fermionic atoms allows interesting manipulations with these dimers. It seems realistic to arrange a deep evaporative cooling of their Bose-condensed gas to temperatures of the order of the chemical potential. Then, converting the molecular BEC into fermionic atoms by adiabatically changing the scattering length to negative values, one provides an additional cooling. The obtained atomic Fermi gas will have extremely low temperatures  $T \sim 10^{-2} E_F$  and can be already in the BCS regime [63]. At these temperatures, one has a very strong Pauli blocking of elastic collisions and expects the collisionless regime for the thermal cloud, which is promising for identifying the BCS-paired state through the observation of collective oscillations or free expansion [64].

Another idea is related to transferring weakly bound molecules of fermionic atoms to their ground rovibrational state by using two-photon spectroscopy, as proposed in Ref. [65] for molecules of bosonic atoms. Long lifetime of weakly bound dimers of fermionic atoms at densities  $\sim 10^{13} \text{ cm}^{-3}$  should provide a much more efficient production of ground-state molecules compared to the case of dimers of bosonic atoms, where one has severe limitations on achievable densities and lifetimes.

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## APPENDIX

We first prove that in the limit  $r_+ \rightarrow 0$  we have Eq. (20) and the integral on the right-hand side of this equation is convergent. So, we consider the integral

$$I = \int G_E[\sqrt{(\mathbf{r} - \mathbf{r}')^2 + r_+^2}][h(\mathbf{r}') - h(\mathbf{r})]d^3r' \quad (\text{A1})$$

and analyze the limiting case of  $r_+ \rightarrow 0$ . For this purpose, we use the expansion of the functions  $h(\mathbf{r}')$  and  $h(\mathbf{r})$  in spherical harmonics. This type of expansion can be made for any function of the components of a three-dimensional vector, and it reads



$$h(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l h_{lm}(r) Y_{lm}(\theta_{\mathbf{r}}, \phi_{\mathbf{r}}), \quad (\text{A2})$$

with  $\theta_{\mathbf{r}}$  and  $\phi_{\mathbf{r}}$  being the polar and azimuthal angles of the vector  $\mathbf{r}$  with respect to a quantization axis. Note that in the analysis of the atom-dimer elastic scattering in Sec. IV, we used an expansion in Legendre polynomials for the function  $f(\mathbf{r})$ . The reason is that the bound molecular state has zero orbital angular momentum and there is a cylindrical symmetry in the system. For a general three-body problem one should, in principle, use Eq. (A2).

For spherical harmonics  $Y_{lm}(\theta_{\mathbf{r}'}, \phi_{\mathbf{r}'})$  in the expansion (A2) for the function  $h(\mathbf{r}')$ , we use the relation (see [42])

$$Y_{lm}(\theta_{\mathbf{r}'}, \phi_{\mathbf{r}'}) = \sum_{m'} D_{m'm}^{(l)}(\phi_{\mathbf{r}}, \theta_{\mathbf{r}}, 0) Y_{lm'}(\theta', \phi'), \quad (\text{A3})$$

where  $D_{m'm}^{(l)}$  is the matrix of finite rotations, and  $\theta'$ ,  $\phi'$  are the polar and azimuthal angles of the vector  $\mathbf{r}'$  with respect to the quantization axis parallel to the vector  $\mathbf{r}$ . Integrating over the angle  $\phi'$  in Eq. (A1), we find that all terms with  $m' \neq 0$  vanish. This is because the argument of the Green function  $G_E$  in Eq. (A1) depends only on the angle  $\theta'$ . Using the relations  $Y_{l0}(\theta', 0) = i^l \sqrt{(2l+1)/4\pi} P_l(\cos \theta')$  and  $D_{0m}^{(l)}(\phi_{\mathbf{r}}, \theta_{\mathbf{r}}, 0) = i^{-l} \sqrt{4\pi/(2l+1)} Y_{lm}(\theta_{\mathbf{r}}, \phi_{\mathbf{r}})$ , we then reduce Eq. (A1) to the form

$$I = \sum_{l=0}^{\infty} \sum_{m=-l}^l I_{lm} Y_{lm}(\theta_{\mathbf{r}}, \phi_{\mathbf{r}}), \quad (\text{A4})$$

$$I_{lm} = 2\pi \int_{-1}^1 d \cos \theta' \int_0^{\infty} r'^2 dr' [h_{lm}(r') P_l(\cos \theta') - h_{lm}(r)] G_E(\sqrt{r^2 + r'^2 + r_+^2 - 2rr' \cos \theta'}). \quad (\text{A5})$$

With Eq. (15) for the Green function  $G_E$ , integration in parts over  $d \cos \theta'$  transforms Eq. (A5) into

$$I_{lm} = \mathcal{A}_{lm} + \int_0^{\infty} \frac{\sqrt{-E} r' dr'}{4\pi^2 r} [h_{lm}(r') - h_{lm}(r)] \times \frac{K_1(\sqrt{-E} \sqrt{(r-r')^2 + r_{\pm}^2})}{\sqrt{(r-r')^2 + r_{\pm}^2}}. \quad (\text{A6})$$

The quantities  $\mathcal{A}_{lm}$  represent the sum of integrals in which for  $r_+ = 0$  and  $r' \rightarrow r$  the integrand either remains finite or contains a logarithmic integrable singularity. Setting  $r_+ = 0$ , one obtains finite values of these quantities,

$$\begin{aligned} \mathcal{A}_{lm} = & \int_0^{\infty} \frac{r'}{r} dr' \frac{[h_{lm}(r) + (-1)^{l+1} h_{lm}(r')] \sqrt{-E}}{4\pi^2 (r+r')} \\ & \times K_1(\sqrt{-E}(r+r')) + \int_0^{\infty} \frac{h_{lm}(r')}{4\pi^2 r^2} dr' \left( \frac{l(l+1)}{2} \right. \\ & \times [K_0(\sqrt{-E}|r-r'|) + (-1)^l K_0(\sqrt{-E}(r+r'))] \\ & \left. - \int_{-1}^1 dx P_l''(x) K_0(\sqrt{-E} \sqrt{r^2 + r'^2 - 2rr'x}) \right). \quad (\text{A7}) \end{aligned}$$

Equations (A6) and (A7) are written for the case  $E < 0$ . For  $E > 0$ , one should put in these equations  $E$  instead of  $-E$  and replace the decaying Bessel functions  $K_1$  and  $K_0$  by the Hankel functions  $2iH_1$  and  $2iH_0$ , respectively.

For calculating the integral in Eq. (A6), we divide the region of integration into two parts: inside a small interval  $\mathcal{L}$ , where  $|r' - r| \ll 1/\sqrt{|E|}$ , and outside this interval. In addition, we require that the function  $h_{lm}(r')$  does not significantly change inside the interval  $\mathcal{L}$ . The integral outside the interval  $\mathcal{L}$  remains finite and independent of  $r_+$  in the limit  $r_+ \rightarrow 0$ . Inside the interval  $\mathcal{L}$ , the argument of the Bessel (or Hankel) function is small and the integral in Eq. (A6) reduces to

$$\frac{1}{4\pi^2} \int_{r' \in \mathcal{L}} \frac{[h_{lm}(r') - h_{lm}(r)] r'}{(r' - r)^2 + r_+^2} dr'.$$

We then expand the quantity  $[h_{lm}(r') - h_{lm}(r)]$  in powers of  $(r' - r)$ . Quadratic and higher-order terms of the expansion give contributions to the integrand, which remain finite for  $r_+ \rightarrow 0$ . The contribution of the linear term is given by

$$\frac{1}{4\pi^2} \frac{dh_{lm}(r)}{dr} \int_{r' \in \mathcal{L}} \frac{r' - r}{(r' - r)^2 + r_+^2} \frac{r'}{r} dr'. \quad (\text{A8})$$

For  $r_+ \rightarrow 0$ , the integral in Eq. (A8) remains finite and can be written as

$$\int_{r' \in \mathcal{L}} \frac{dr'}{r} + \text{P} \int_{r' \in \mathcal{L}} \frac{dr'}{(r' - r)},$$

where the symbol P denotes the principal value of the integral. We thus see that in the limit  $r_+ \rightarrow 0$  the whole integral  $I$  given by Eq. (A1) is finite. Setting  $r_+ = 0$  in the initial expression (A1) and keeping the symbol P for the integration over  $dr'$ , one then writes the integral  $I$  in the form of Eq. (20),

$$I = \text{P} \int G_E(|\mathbf{r} - \mathbf{r}'|) [h(\mathbf{r}') - h(\mathbf{r})] d^3 r'.$$

We now derive Eq. (62) for the four-body problem of the dimer-dimer scattering and prove that the integral in the second line of this equation is convergent. So, changing the notation from  $\mathbf{r}_2$  to  $\mathbf{r}$ , we start with the integral

$$J = \int d^3 r' d^3 \mathbf{R}' [h(\mathbf{r}', \mathbf{R}') - h(\mathbf{r}, \mathbf{R})] G(|S - S_1|), \quad (\text{A9})$$

where the argument of the Green function in Eq. (A9) is

$$|S - S_1| = \sqrt{r_1^2 + (\mathbf{r} - \mathbf{r}')^2 + (\mathbf{R} - \mathbf{R}')^2},$$

and consider the limit  $r_1 \rightarrow 0$ . As in the three-body case, we expand the function  $h(\mathbf{r}, \mathbf{R})$  in spherical harmonics. The expansion now reads

$$\begin{aligned} h(\mathbf{r}, \mathbf{R}) = & \sum_{l=0, l'=0}^{\infty} \sum_{m=-l}^l \sum_{m'=-l'}^{l'} h_{lm}^{l'm'}(r, R) \\ & \times Y_{lm}(\theta_{\mathbf{r}}, \phi_{\mathbf{r}}) Y_{l'm'}(\theta_{\mathbf{R}}, \phi_{\mathbf{R}}), \quad (\text{A10}) \end{aligned}$$

where  $\theta_{\mathbf{r}}$ ,  $\phi_{\mathbf{r}}$  and  $\theta_{\mathbf{R}}$ ,  $\phi_{\mathbf{R}}$  are the polar and azimuthal angles of the vectors  $\mathbf{r}$  and  $\mathbf{R}$ . Then, using Eq. (A3) for each of the



spherical harmonics in the expansion of the function  $h(\mathbf{r}', \mathbf{R}')$ , we transform Eq. (A9) to the form

$$J = \sum_{l=0, l'=0}^{\infty} \sum_{m=-l}^l \sum_{m'=-l'}^{l'} J_{lm}^{l'm'} Y_{lm}(\theta_{\mathbf{r}}, \phi_{\mathbf{r}}) Y_{l'm'}(\theta_{\mathbf{R}}, \phi_{\mathbf{R}}), \quad (\text{A11})$$

$$\begin{aligned} J_{lm}^{l'm'} &= 4\pi^2 \int_{-1}^1 d \cos \theta'_{\mathbf{r}} \int_{-1}^1 d \cos \theta'_{\mathbf{R}} \int_0^{\infty} r'^2 dr' \int_0^{\infty} R'^2 dR' \\ &\times [h_{lm}^{l'm'}(r', R') P_l(\cos \theta'_{\mathbf{r}}) P_{l'}(\cos \theta'_{\mathbf{R}}) \\ &- h_{lm}^{l'm'}(r, R)] G(X), \end{aligned} \quad (\text{A12})$$

with the angle between the vectors  $\mathbf{r}'$  and  $\mathbf{r}$  denoted as  $\theta'_{\mathbf{r}}$ , the angle between  $\mathbf{R}'$  and  $\mathbf{R}$  as  $\theta'_{\mathbf{R}}$ , and the argument of the Green function written as

$$X = \sqrt{r_1^2 + r^2 + r'^2 - 2rr' \cos \theta'_{\mathbf{r}} + R^2 + R'^2 - 2RR' \cos \theta'_{\mathbf{R}}}.$$

We then separate out the region of integration  $\tilde{V}$ , where the angles  $\theta'_{\mathbf{r}}$  and  $\theta'_{\mathbf{R}}$  are small,  $r'$  is close to  $r$ , and  $R'$  is close to  $R$ . The region  $\tilde{V}$  is determined by the relations

$$|r' - r| \leq r_0 \ll r', r, a, \quad (\text{A13})$$

$$|R' - R| \leq r_0 \ll R', R, a, \quad (\text{A14})$$

$$\theta'_{\mathbf{r}} \leq \eta_{\mathbf{r}} \ll \min\{1, a/\sqrt{rr'}\}, \quad (\text{A15})$$

$$\theta'_{\mathbf{R}} \leq \eta_{\mathbf{R}} \ll \min\{1, a/\sqrt{RR'}\}, \quad (\text{A16})$$

and the quantities  $\eta_{\mathbf{r}}, \eta_{\mathbf{R}}$  are selected such that they satisfy the inequalities

$$\eta_{\mathbf{r}} \sqrt{rr'} \gg |r' - r|, \quad (\text{A17})$$

$$\eta_{\mathbf{R}} \sqrt{RR'} \gg |R' - R|. \quad (\text{A18})$$

Outside the region  $\tilde{V}$ , one can directly put  $r_1=0$  in the argument of the Green function and see that the quantities  $J_{lm}^{l'm'}$  remain finite. These contributions are denoted below as  $\bar{J}_{lm}^{l'm'}$ . In the region  $\tilde{V}$ , the argument  $X$  of the Green function can become equal to  $r_1$  and, in principle, this region can be thought of as the one leading to a singular behavior of the integral  $J$  in the limit  $r_1 \rightarrow 0$ . We will show that this is not the case.

The Green function  $G$  is given by Eq. (58), and in the region  $\tilde{V}$  the argument of the decaying Bessel function,  $\sqrt{2}X/a$ , is small. Then, for small angles  $\theta_{\mathbf{r}}$  and  $\theta_{\mathbf{R}}$ , from Eq. (58) we obtain

$$G = \frac{15}{32\pi^4} [r_1^2 + (r' - r)^2 + (R' - R)^2 + \theta_{\mathbf{r}}^2 rr' + \theta_{\mathbf{R}}^2 RR']^{-7/2}. \quad (\text{A19})$$

Inside the region  $\tilde{V}$ , the inequalities (A15) and (A16) allow us to put  $P_l(\cos \theta'_{\mathbf{r}}) = P_{l'}(\cos \theta'_{\mathbf{R}}) = 1$  in Eq. (A12). On the

other hand, owing to the inequalities (A17) and (A18), we can put infinity for the upper limits of integration over  $\theta'_{\mathbf{r}}$  and  $\theta'_{\mathbf{R}}$ . Then, integrating over the angles inside the region  $\tilde{V}$  and taking into account the contribution  $\bar{J}_{lm}^{l'm'}$  from the configuration space outside this region, we reduce Eq. (A12) to

$$\begin{aligned} J_{lm}^{l'm'} &= \bar{J}_{lm}^{l'm'} + \frac{1}{8\pi^2} \int_{r', R' \in \tilde{V}} \frac{r' R'}{r R} dr' dR' \\ &\times \frac{[h_{lm}^{l'm'}(r', R') - h_{lm}^{l'm'}(r, R)]}{[r_1^2 + (r' - r)^2 + (R' - R)^2]^{3/2}}. \end{aligned} \quad (\text{A20})$$

For calculating the integral in Eq. (A20), we expand the function  $h(r', R')$  in powers of  $(r' - r)$  and  $(R' - R)$ . Quadratic and higher-order terms of the expansion lead to the integrand which remains finite for  $r_1 \rightarrow 0$ , at least after a straightforward integration over one of the variables,  $r'$  or  $R'$ . For example, setting  $r_1=0$ , quadratic terms yield

$$\begin{aligned} &\frac{\partial^2 h_{lm}^{l'm'}(r, R)}{8\pi^2 \partial r^2} \int_{r' \in \tilde{V}} \frac{r_0 dr'}{[r_0^2 + (r' - r)^2]^{1/2}} + \frac{\partial^2 h_{lm}^{l'm'}(r, R)}{8\pi^2 \partial R^2} \\ &\times \int_{R' \in \tilde{V}} \frac{r_0 dR'}{[r_0^2 + (R' - R)^2]^{1/2}} + \frac{\partial^2 h_{lm}^{l'm'}(r, R)}{4\pi^2 \partial r \partial R} \int_{r' \in \tilde{V}} \frac{dr' (r' - r)^2}{r R} \\ &\times \left[ \ln \left( \frac{r_0 + \sqrt{r_0^2 + (r' - r)^2}}{|r' - r|} \right) - \frac{r_0}{[r_0^2 + (r' - r)^2]^{1/2}} \right]. \end{aligned}$$

The contribution of the linear terms of the expansion, after integrating over  $R'$ , can be written as

$$\begin{aligned} &\frac{\partial h_{lm}^{l'm'}(r, R)}{4\pi^2 r \partial r} \int_{r' \in \tilde{V}} \frac{(r' - r)}{r_1^2 + (r' - r)^2} \frac{r_0 r' dr'}{[r_0^2 + (r' - r)^2]^{1/2}} \\ &+ \frac{\partial h_{lm}^{l'm'}(r, R)}{4\pi^2 R \partial R} \int_{r' \in \tilde{V}} \frac{r' dr'}{r} \left[ \ln \left( \frac{r_0 + \sqrt{r_0^2 + (r' - r)^2}}{|r' - r|} \right) \right. \\ &\left. - \frac{r_0}{[r_0^2 + (r' - r)^2]^{1/2}} \right], \end{aligned} \quad (\text{A21})$$

where we put  $r_1=0$  in the second integral as it then contains only an integrable logarithmic singularity for  $r' \rightarrow r$ . The first integral on the right-hand side of Eq. (A21) also remains finite in the limit of  $r_1 \rightarrow 0$ . It can be written in the form

$$\int_{r' \in \tilde{V}} \frac{r_0 dr'}{[r_0^2 + (r' - r)^2]^{1/2}} + \text{P} \int_{r' \in \tilde{V}} \frac{r dr'}{(r' - r)} \frac{r_0}{[r_0^2 + (r' - r)^2]^{1/2}},$$

with the symbol P denoting the principal value of the integral. This means that setting  $r_1=0$ , each of the quantities  $J_{lm}^{l'm'}$  is equal to the principal value of the integral in Eq.

(A12), taken with respect to the integration over  $dr'$ . Note that we could first make the integration over  $dr'$  and reduce the result to the principal value for the integration over  $dR'$ . One thus sees that for  $r_1 \rightarrow 0$ , the initial integral  $J$  (A9) can be represented in the form of Eq. (62),

$$J = P \int d^3r' d^3R' [h(\mathbf{r}', \mathbf{R}') - h(\mathbf{r}, \mathbf{R})] G(|\bar{S} - S_1|),$$

where the symbol  $P$  denotes the principal value for the integration over  $dr'$  (or  $dR'$ ), and  $|\bar{S} - S_1| = \sqrt{(\mathbf{r} - \mathbf{r}')^2 + (\mathbf{R} - \mathbf{R}')^2}$ .

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