

# Diatomic molecules in ultracold Fermi gases—novel composite bosons

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## Abstract

We give a brief overview of recent studies of weakly bound homonuclear molecules in ultracold two-component Fermi gases. It is emphasized that they represent novel composite bosons, which exhibit features of Fermi statistics at short intermolecular distances. In particular, the Pauli exclusion principle for identical fermionic atoms provides a strong suppression of collisional relaxation of such molecules into deep bound states. We then analyse heteronuclear molecules which are expected to be formed in mixtures of different fermionic atoms. We show how an increase in the mass ratio for the constituent atoms changes the physics of collisional stability of such molecules compared to homonuclear ones. We discuss Bose–Einstein condensation of these composite bosons and consider prospects for future studies.

## 1. Introduction

Quantum statistics for bosons and fermions forms the basis of our understanding of many-body physics. In the case of a dilute gas of bosons, one faces the phenomenon of Bose–Einstein condensation (BEC), a macroscopic occupation of a single quantum state below a certain critical temperature, predicted by Bose and Einstein in 1924 [1, 2]. The idea of BEC originally comes from the analogy between light and matter waves. Indeed, at sufficiently low temperatures the de Broglie wavelength of particles exceeds the mean inter-particle separation, and the wave packets of particles start overlapping. Then quantum statistics comes into play and it becomes favourable for bosons to occupy a single quantum state. This state represents a macroscopic quantum object called a Bose–Einstein condensate, and the formation of the condensate manifests itself as a phase transition accompanied by a change in some of the properties of the gas.

Since the work of Bose [1] and Einstein [2], a number of phenomena in interacting systems have been considered as manifestations of BEC: superfluidity in liquid helium, high- $T_c$  superconductivity in some materials, condensation of hypothetical Higgs particles, BEC of pions and so on. Bose–Einstein condensation in dilute gases was first observed in 1995 in pioneering experiments with clouds of magnetically trapped alkali atoms at JILA [3], MIT [4] and Rice [5]. The first generation of studies of trapped Bose-condensed gases found a variety of spectacular macroscopic quantum effects: interference between two condensates, collective oscillations and their damping, formation of quantized vortices and vortex lattices, atom lasers, etc (see [6] for a review).

In the last few years, the field of quantum gases is strongly expanding in the direction of ultracold two-component clouds of fermionic atoms, with the initial goal of achieving a superfluid Bardeen–Cooper–Schrieffer (BCS) phase transition. This transition requires attractive interaction between the atoms. Then, in the simplest version of the superfluid transition, at sufficiently low temperatures fermions belonging to different components and having opposite momenta on the Fermi surface form correlated (Cooper) pairs in the momentum space. This leads to the appearance of a gap in the excitation spectrum and to the phenomenon of superfluidity (see, for example, [7]). In a dilute ultracold two-component Fermi gas, most efficient is the formation of Cooper pairs due to the attractive intercomponent interaction in the  $s$ -wave channel (negative  $s$ -wave scattering length  $a$ ). However, for ordinary values of  $a$ , the superfluid transition temperature is extremely low.

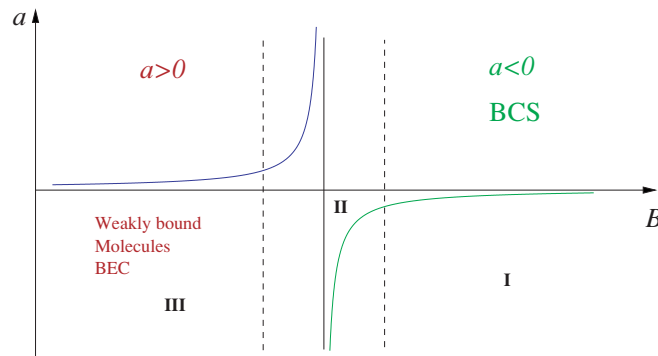
For this reason, the efforts of experimental groups have been focused on modifying the intercomponent interaction by using Feshbach resonances (see below). In this case, one can switch the sign and tune the absolute value of  $a$ , which at resonance changes from  $+\infty$  to  $-\infty$ . This has led to remarkable developments, in particular to the creation of weakly bound diatomic molecules of fermionic atoms on the positive side of the resonance ( $a > 0$ ) [8–11]. These are the largest diatomic molecules obtained so far. Their size is of the order of  $a$  and it reaches hundreds of nanometres in current experiments. Accordingly, their binding energy is exceedingly small ( $10^{-10}$  eV or less). Being composite bosons, these molecules obey Bose statistics, and they have been Bose-condensed in JILA experiments with  $^{40}\text{K}_2$  [12, 13] and in  $^6\text{Li}_2$  experiments at Innsbruck [14, 15], MIT [16, 17], ENS [18] and Rice [19].

Nevertheless, some of the interaction properties of these molecules reflect Fermi statistics of the individual atoms forming the molecule. In particular, these molecules are found remarkably stable with respect to collisional decay. Being in the highest rovibrational state, they do not undergo collisional relaxation to deeply bound states on a time scale exceeding seconds at densities of about  $10^{13}\text{ cm}^{-3}$ , which is more than four orders of magnitude longer than the lifetime of similar molecules consisting of bosonic atoms.

Currently, a new generation of experiments is being set up for studying degenerate mixtures of different fermionic atoms, where one expects the formation of heteronuclear weakly bound molecules. In this paper, we analyse elastic interaction between these molecules and their collisional relaxation to deeply bound states. The emphasis is put on the dependence of these properties on the mass ratio for the constituent atoms and on the comparison of the results with those for presently studied homonuclear molecules. We present a physical picture of how such composite bosons can exhibit features of Fermi statistics and show that this is the reason for their collisional stability.

## 2. Feshbach resonances and diatomic molecules in cold Fermi gases

The studies of interacting quantum gases are actively pursued using Feshbach resonances, in particular for tuning and increasing the intercomponent interaction in two-species Fermi



**Figure 1.** The dependence of the scattering length on the magnetic field. The symbols I, II and III stand for the regime of a weakly interacting atomic Fermi gas, the strongly correlated regime and the regime of weakly bound molecules. At low enough temperatures region I corresponds to the BCS superfluid pairing, and region III to Bose–Einstein condensation of molecules.

gases. In the vicinity of the resonance, for the two-particle problem one has strong coupling between (zero-energy) continuum states of colliding atoms and a bound molecular state of another hyperfine manifold. The effective coupling strength depends on the detuning from the resonance (the energy difference  $\delta$  between the bound molecular state and the continuum states), which can be varied by changing the magnetic field. Thus, the scattering length becomes field dependent (see figure 1).

At resonance the scattering length changes from  $+\infty$  to  $-\infty$ , and in the vicinity of the resonance one has the inequality  $k_F|a| \gtrsim 1$  where  $k_F$  is the Fermi momentum. The gas is then in the strongly interacting regime. It is still dilute and the mean interparticle separation greatly exceeds the characteristic radius of interparticle interaction  $R_e$ . However, the amplitude of binary interactions (scattering length) is larger than the mean separation between particles, and the ordinary mean field approach is no longer valid.

For a large detuning from resonance the gas is still in the weakly interacting regime, i.e. the inequality  $n|a|^3 \ll 1$  is satisfied, where  $n$  is the density of the gas. On the negative side of the resonance ( $a < 0$ ), at sufficiently low temperatures of a two-component atomic Fermi gas one expects BCS pairing between distinguishable fermions, well described in the literature [7]. On the positive side ( $a > 0$ ), two fermions belonging to different components form weakly bound molecules. The collisional stability and Bose–Einstein condensation of these molecules is a subtle question, and it is the main topic of this paper.

The idea of resonance coupling through a Feshbach resonance for achieving a superfluid phase transition in ultracold two-component Fermi gases was proposed in [20, 21]. The crossover from the BCS to BEC behaviour now attracts a great deal of interest, in particular with respect to the nature of superfluid pairing, transition temperature and elementary excitations. It is worth noting that this type of crossover has been discussed in the literature in the context of superconductivity [22–25] and in relation to superfluidity in two-dimensional films of  $^3\text{He}$  [26, 27].

The description of a many-body system near a Feshbach resonance requires a detailed knowledge of the two-body problem. This is a two-channel problem which can be described in terms of Breit–Wigner scattering [28, 29], 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 problems have been discussed by Feshbach [30] and Fano [31]. In cold atom physics, the idea of Feshbach resonances was introduced in [32], and optically induced resonances have been discussed in [33, 34].

The two-body physics is the most transparent if one can omit the (small) background scattering length. Then for low collision energies  $\varepsilon$  the scattering amplitude is given by [29]

$$F(\varepsilon) = -\frac{\hbar\gamma/\sqrt{2\mu}}{\varepsilon + \delta + i\gamma\sqrt{\varepsilon}}, \quad (1)$$

where the quantity  $\hbar\gamma/\sqrt{2\mu} \equiv W$  characterizes the coupling between the two hyperfine domains and  $\mu$  is the reduced mass of the two atoms. The scattering length is  $a = -F(0)$ . In equation (1) the detuning  $\delta$  is positive if the bound molecular state is below the continuum of colliding atoms. Then for  $\delta > 0$  the scattering length is positive, and for  $\delta < 0$  it is negative. Introducing a characteristic length

$$R^* = \hbar^2/2\mu W \quad (2)$$

and expressing the scattering amplitude through the relative momentum of particles  $k = \sqrt{2\mu\varepsilon}/\hbar$ , equation (1) takes the form:

$$F(k) = -\frac{1}{a^{-1} + R^*k^2 + ik}. \quad (3)$$

The validity of equation (3) does not require the inequality  $kR^* \ll 1$ . At the same time, this equation formally coincides with the amplitude of scattering of slow particles by a potential with the same scattering length  $a$  and an effective range  $R = -2R^*$ , obtained under the condition  $k|R| \ll 1$ .

The length  $R^*$  is an intrinsic parameter of the Feshbach resonance problem. It characterizes the width of the resonance. From equations (1) and (2) 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 discussed in the literature [35–42].

In fact, the use of the terms ‘wide’ and ‘narrow’ depends on the problem under consideration. For example, in the unitarity limit where  $a \rightarrow \pm\infty$ , equation (3) 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  $k_F = (3\pi^2n)^{1/3}$ . Thus, for a given  $R^*$  the condition of the wide resonance depends on the gas density  $n$  and takes the form  $k_F R^* \ll 1$  [37, 38, 40–42]. Then the scattering properties of the gas are the same as in the case of potential scattering at an infinite scattering length.

For  $a > 0$  and  $na^3 \ll 1$ , where one has a weakly interacting gas of diatomic bosonic molecules [43], the criterion of the wide resonance is different [39, 44]. The most important limitation is related to the binding energy and the wavefunction of the molecules. The energy of the weakly bound molecular state (it is certainly assumed that the characteristic radius of interaction  $R_e \ll a$ ) is determined by the pole of the scattering amplitude (3). One then finds [39, 44] that this state exists only for  $a > 0$  and under the condition

$$R^* \ll a, \quad (4)$$

the binding energy is given by

$$\varepsilon_0 = \hbar^2/2\mu a^2. \quad (5)$$

Then the wavefunction of the weakly bound molecular state has only a small admixture of the closed channel, the size of the molecule is  $\sim a$  and atom–molecule and molecule–molecule interactions are determined by a single parameter—the atom–atom scattering length  $a$ . In this sense, the problem becomes universal. It is equivalent to the interaction problem for the two-body potential which is characterized by a large positive scattering length  $a$  and has a potential well with a weakly bound molecular state. The picture remains the same when

the background scattering length  $a_{bg}$  cannot be neglected, although the condition of a wide resonance can be somewhat modified [45].

Experimental studies are currently dealing with Fermi gases consisting of atoms in two different internal (hyperfine) states and, accordingly, having equal masses. Most experiments use wide Feshbach resonances. For example, weakly bound molecules  ${}^6\text{Li}_2$  and  ${}^{40}\text{K}_2$  have been produced in experiments [9–19] by using Feshbach resonances with a length  $R^*$  of the order of or smaller than 20 Å. Then, for the achieved values of the scattering length  $a$  from 500 to 2000 Å, 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 G [46]. For this resonance the length  $R^*$  is very large and at obtained values of  $a$  condition (4) is not fulfilled. Below we will focus attention on the case of a wide Feshbach resonance.

### 3. Elastic interaction between weakly bound molecules

At temperatures sufficiently lower than the molecular binding energy  $\varepsilon_0$  and for equal concentrations of the two atomic components, practically all atoms are converted into molecules if the gas density satisfies the inequality  $na^3 \ll 1$  [47]. This will definitely be the case at temperatures well below the Fermi energy (the lowest of the two Fermi energies in the case of atoms with different masses). Thus, one has a molecular Bose gas and the first key question is the elastic interaction (scattering) between the molecules. It is important for evaporative cooling of the molecular gas to the regime of Bose–Einstein condensation and for the stability of the condensate. In the latter respect, the elastic interaction should be repulsive, otherwise the Bose-condensed molecular gas undergoes a collapse.

The exact solution for the molecule–molecule elastic scattering in the case of equal atom masses was found in [43], and a detailed analysis of this problem was given in [44]. This was done assuming that the (positive) atom–atom scattering length  $a$  for the interspecies interaction greatly exceeds the characteristic radius of interatomic potential:

$$a \gg R_e. \quad (6)$$

Then, as in the case of the three-body problem with fermions [48–51], the amplitude of elastic interaction is determined only by  $a$  and can be found in the zero-range approximation for the interatomic potential.

This approach was introduced in the two-body physics by Bethe and Peierls [52]. The leading idea is to solve the equation for the free relative motion of two particles placing a boundary condition on the wavefunction  $\psi$  at a vanishing interparticle distance  $r$ :

$$\frac{(r\psi)'}{r\psi} = -\frac{1}{a}, \quad r \rightarrow 0, \quad (7)$$

which can also be rewritten as

$$\psi \propto (1/r - 1/a), \quad r \rightarrow 0. \quad (8)$$

One then gets a correct expression for the wavefunction at distances  $r \gg R_e$ . For the case where  $a \gg R_e$ , equation (8) gives a correct result for the wavefunction of weakly bound and continuum states even at distances much smaller than  $a$ .

In this section, we generalize the results on the molecule–molecule scattering obtained in [43, 44] to the case of molecules consisting of fermionic atoms with different masses  $M$  and  $m$  ( $m < M$ ). This is relevant for weakly bound heteronuclear molecules, such as  ${}^6\text{Li}$ - ${}^{40}\text{K}$ ,  ${}^6\text{Li}$ - ${}^{87}\text{Sr}$ ,  ${}^{40}\text{K}$ - ${}^{173}\text{Yb}$  etc, which can be formed by sweeping across a Feshbach resonance for the interspecies interaction. Elastic interaction between such molecules is important for

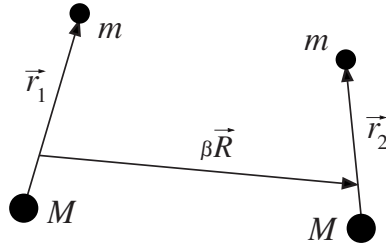


Figure 2. Set of coordinates for the four-body problem.

understanding the physics of their Bose–Einstein condensation and for studying the BCS–BEC crossover in Fermi mixtures.

The ultracold limit for the molecule–molecule scattering is realized under the condition  $ka \ll 1$ , where  $k$  is the relative momentum. This is because  $a$  is approximately the range of interaction between the molecules. In this case, the scattering is dominated by the contribution of the  $s$ -wave channel. The inequality  $ka \ll 1$  is equivalent to the collision energy much smaller than the molecular binding energy  $\varepsilon_0$ . Hence, the  $s$ -wave molecule–molecule elastic scattering can be analysed putting the total energy equal to  $-2\varepsilon_0 = -\hbar^2/\mu a^2$ . In the zero-range approximation one should solve the four-body free-particle Schrödinger equation:

$$[-\nabla_{\mathbf{r}_1}^2 - \nabla_{\mathbf{r}_2}^2 - \nabla_{\mathbf{R}}^2 + 2/a^2]\Psi = 0, \quad (9)$$

placing the Bethe–Peierls boundary condition at vanishing distances between heavy and light fermions. In equation (9) the distance between two given heavy and light fermions is  $\mathbf{r}_1$ , and  $\mathbf{r}_2$  is the distance between the other two (see figure 2). The distance between the centres of mass of these pairs is  $\beta\mathbf{R}$ , and  $\mathbf{r}_{\pm} = \alpha_{\pm}\mathbf{r}_1 + \alpha_{\mp}\mathbf{r}_2 \pm \beta\mathbf{R}$  are the separations between heavy and light fermions in the other two possible heavy–light pairs. Here we introduced constants  $\beta = \sqrt{2\alpha_+\alpha_-}$ ,  $\alpha_+ = \mu/M$ ,  $\alpha_- = \mu/m$ , and the reduced mass is  $\mu = mM/(m+M)$ .

The wavefunction  $\Psi$  is symmetric with respect to the permutation of composite bosons and antisymmetric with respect to permutations of identical fermions:

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) &= \Psi(\mathbf{r}_2, \mathbf{r}_1, -\mathbf{R}) \\ &= -\Psi(\mathbf{r}_{\pm}, \mathbf{r}_{\mp}, \pm\beta(\mathbf{r}_1 - \mathbf{r}_2) \mp (\alpha_+ - \alpha_-)\mathbf{R}). \end{aligned} \quad (10)$$

The Bethe–Peierls boundary condition should be placed for a vanishing distance in any pair of heavy and light fermions, i.e. for  $\mathbf{r}_1 \rightarrow 0$ ,  $\mathbf{r}_2 \rightarrow 0$  and  $\mathbf{r}_{\pm} \rightarrow 0$ . Due to the symmetry it is necessary to require a proper behaviour of  $\Psi$  only at one of these boundaries. For  $\mathbf{r}_1 \rightarrow 0$  the boundary condition reads

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) \rightarrow f(\mathbf{r}_2, \mathbf{R})(1/4\pi r_1 - 1/4\pi a). \quad (11)$$

The function  $f(\mathbf{r}_2, \mathbf{R})$  contains the information about the second pair of particles when the first two are on top of each other.

For large  $R$  the wavefunction  $\Psi$  is given by

$$\Psi \approx \phi_0(r_1)\phi_0(r_2)(1 - a_{\text{dd}}/\beta R); \quad R \gg a, \quad (12)$$

where  $a_{\text{dd}}$  is the molecule–molecule scattering length, and the wavefunction of the weakly bound molecule is given by

$$\phi_0(r) = (r\sqrt{2\pi a})^{-1} \exp(-r/a). \quad (13)$$

Combining equations (11) and (12) we obtain the asymptotic expression for  $f$  at large distances  $R$ :

$$f(\mathbf{r}_2, \mathbf{R}) \approx (2/r_2 a) \exp(-r_2/a)(1 - a_{\text{dd}}/\beta R); \quad R \gg a. \quad (14)$$

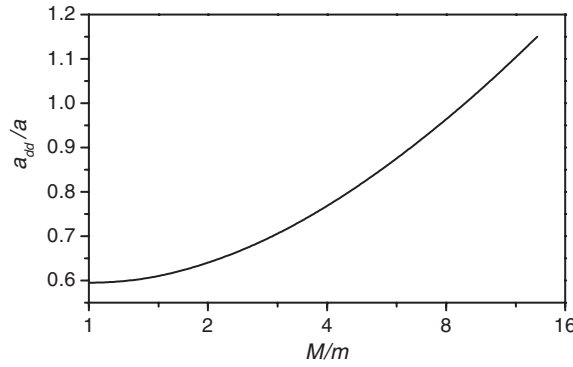


Figure 3. The ratio  $a_{dd}/a$  versus  $M/m$ .

For 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. An equation for the function  $f$  in the case  $m = M$  is derived in [43, 44]. The generalization of this approach to the case of different masses is straightforward and we obtain the same integral equation:

$$\int_{\mathbf{r}', \mathbf{R}'} \left\{ G(|\bar{S}_1 - S_1|) [f(\mathbf{r}', \mathbf{R}') - f(\mathbf{r}, \mathbf{R})] + \left[ G(|\bar{S}_1 - S_2|) - \sum_{\pm} G(|\bar{S}_1 - S_{\pm}|) \right] f(\mathbf{r}', \mathbf{R}') \right\} = \frac{(\sqrt{2} - 1)f(\mathbf{r}, \mathbf{R})}{4\pi a}. \quad (15)$$

The nine-dimensional vectors  $S_1, S_2$  and  $\bar{S}_1$  are again given by  $S_1 = \{0, \mathbf{r}', \mathbf{R}'\}$ ,  $S_2 = \{\mathbf{r}', 0, -\mathbf{R}'\}$ ,  $\bar{S}_1 = \{0, \mathbf{r}, \mathbf{R}\}$ , and  $G(x) = (2\pi)^{-9/2} (xa/\sqrt{2})^{-7/2} K_{7/2}(\sqrt{2}x/a)$  is the Green function of equation (9), with  $K_{7/2}$  being the decaying Bessel function. The effect of different masses is contained in the expressions for the vectors  $S_{\pm}$ , which now read  $S_{\pm} = \{\alpha_{\mp}\mathbf{r}' \pm \beta\mathbf{R}', \alpha_{\pm}\mathbf{r}' \mp \beta\mathbf{R}', \mp\beta\mathbf{r}' \mp (\alpha_{+} - \alpha_{-})\mathbf{R}'\}$ .

It is more convenient to make calculations in the momentum space, transforming equation (15) into an equation for the function  $f(\mathbf{k}, \mathbf{p}) = \int d^3r d^3R f(\mathbf{r}, \mathbf{R}) \exp(i\mathbf{k} \cdot \mathbf{r}/a + i\beta\mathbf{p} \cdot \mathbf{R}/a)$ :

$$\sum_{\pm} \int \frac{f(\mathbf{k} \pm \alpha_{\mp}(\mathbf{p}' - \mathbf{p}), \mathbf{p}') d^3p'}{2 + \beta^2 p'^2 + (\mathbf{k} \pm \alpha_{\mp}(\mathbf{p}' - \mathbf{p}))^2 + (\mathbf{k} \pm \alpha_{\pm}(\mathbf{p}' + \mathbf{p}))^2} = \int \frac{f(\mathbf{k}', -\mathbf{p}) d^3k'}{2 + k'^2 + k^2 + \beta^2 p^2} - \frac{2\pi^2(1 + k^2 + \beta^2 p^2)f(\mathbf{k}, \mathbf{p})}{\sqrt{2 + k^2 + \beta^2 p^2} + 1}. \quad (16)$$

By making the substitution  $f(\mathbf{k}, \mathbf{p}) = (\delta(\mathbf{p}) + g(\mathbf{k}, \mathbf{p})/p^2)/(1 + k^2)$  we reduce equation (16) to an inhomogeneous equation for the function  $g(\mathbf{k}, \mathbf{p})$ . For  $\mathbf{p} \rightarrow 0$  this function tends to a finite value independent of  $\mathbf{k}$ . The molecule–molecule scattering length is given by  $a_{dd} = -2\pi^2 a \lim_{\mathbf{p} \rightarrow 0} g(\mathbf{k}, \mathbf{p})$ , and we have calculated this quantity numerically from equation (16).

In figure 3 we display the ratio  $a_{dd}/a$  versus the mass ratio  $M/m$ . For  $m = M$  we recover the result of [43, 44]:  $a_{dd} = 0.6a$ . Compared to earlier studies which were assuming  $a_{dd} = 2a$  [25], this exact result gives almost twice as small a sound velocity of the molecular condensate and a rate of elastic collisions smaller by an order of magnitude. An approximate diagrammatic approach has been developed in [53], and it has led to  $a_{dd} = 0.75a$ .

The universal dependence of  $a_{\text{dd}}/a$  on the mass ratio, presented in figure 3, can be established in the zero-range approximation only if  $M/m$  is smaller than approximately 13.6. Calculations then show the absence of four-body weakly bound states, and for  $M/m \sim 1$  the behaviour of  $f$  suggests a soft-core repulsion between molecules, with a range  $\sim a$ . For the mass ratio larger than the critical value, the description of the molecule–molecule scattering requires a three-body parameter coming from the short-range behaviour of the three-body subsystem consisting of one light and two heavy fermions [48, 49].

#### 4. Born–Oppenheimer approach

In the case of large  $M/m$ , one can develop a transparent physical picture of the molecule–molecule interaction by using the Born–Oppenheimer approximation [54]. In this case, heavy fermionic atoms are moving slowly in the field produced by the exchange of fast light atoms. The adiabatic behaviour assumes that the four-body problem can be split into two parts. First, we calculate the wavefunctions and binding energies of two light fermions in the field of two heavy atoms fixed at their positions  $\mathbf{x}_1$  and  $\mathbf{x}_2$ . As the motion of heavy atoms is slow, the bound states of the light atoms adiabatically adjust themselves to a given value of the separation between the heavy ones,  $x = |\mathbf{x}_1 - \mathbf{x}_2|$ . The sum of the corresponding binding energies gives the effective interaction potential  $U_{\text{eff}}(x)$  for the heavy fermions. An obvious second step is to solve the Schrödinger equation for their motion in this effective potential.

For  $x > a$ , there are two bound states of a light atom interacting with a pair of fixed heavy atoms. The wavefunctions of these states are given by

$$\psi_{\mathbf{x},\pm}(\mathbf{y}) \propto \left( \frac{e^{-\kappa_{\pm}(x)|\mathbf{y}-\mathbf{x}_1|/x}}{|\mathbf{y}-\mathbf{x}_1|} \pm \frac{e^{-\kappa_{\pm}(x)|\mathbf{y}-\mathbf{x}_2|/x}}{|\mathbf{y}-\mathbf{x}_2|} \right), \quad (17)$$

where  $\mathbf{y}$  is the coordinate of the light atom. The functions  $\kappa_{\pm}(x) > 0$  are determined by the requirement that for  $\mathbf{y} \rightarrow \mathbf{x}_{1,2}$  the wavefunction (17) satisfies the Bethe–Peierls boundary condition (8) in which  $r$  is substituted by  $|\mathbf{y} - \mathbf{x}_{1,2}|$ . This gives algebraic equations:

$$\kappa_{\pm}(x) \mp e^{-\kappa_{\pm}(x)} = x/a. \quad (18)$$

The energies of the bound states are given by

$$\varepsilon_{\pm}(x) = -\hbar^2 \kappa_{\pm}^2(x)/2mx^2. \quad (19)$$

Since the light fermions are identical, their two-body wavefunction can be constructed as an antisymmetrized product of  $\psi_{\mathbf{x},+}$  and  $\psi_{\mathbf{x},-}$ :

$$\psi_{\mathbf{x}}(\mathbf{y}_1, \mathbf{y}_2) \propto \psi_{\mathbf{x},+}(\mathbf{y}_1)\psi_{\mathbf{x},-}(\mathbf{y}_2) - \psi_{\mathbf{x},+}(\mathbf{y}_2)\psi_{\mathbf{x},-}(\mathbf{y}_1), \quad (20)$$

and their total energy is  $U_{\text{eff}}(x) = \varepsilon_+(x) + \varepsilon_-(x)$ . Note that the wavefunction (20) is antisymmetric with respect to the transformation  $\mathbf{x} \rightarrow -\mathbf{x}$ . This means that solving the Schrödinger equation for the heavy fermions,

$$\left[ -\frac{\hbar^2}{M} \nabla_{\mathbf{x}}^2 + U_{\text{eff}}(x) \right] \chi(\mathbf{x}) = E \chi(\mathbf{x}), \quad (21)$$

we have to look for a solution that is symmetric with respect to their permutation (in our case it corresponds to the s-wave scattering). Then the total four-body wavefunction  $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{y}_1, \mathbf{y}_2) \propto \chi(\mathbf{x})\psi_{\mathbf{x}}(\mathbf{y}_1, \mathbf{y}_2)$  has a proper symmetry.

Solving equations (18) at distances  $x > a$  gives a purely repulsive potential monotonically decreasing with  $x$ . At distances  $x \gg a$  it behaves as

$$U_{\text{eff}}(x) \approx -2\varepsilon_0 + (2\hbar^2/m) \exp(-2x/a)/ax; \quad x \gg a. \quad (22)$$



We see that the ratio of the  $x$ -dependent part of the effective repulsion to the kinetic energy term in equation (21) increases with  $M/m$ . This is consistent with exact calculations based on equations (15) and (16).

The Born–Oppenheimer approach fails at distances close to  $a$  as the energy  $\varepsilon_-(x)$  vanishes at  $x = a$ , and the atom in the state ‘–’ moves slower than the heavy atoms. This leads to a contradiction with the adiabatic approximation. However, we see that the light atom in the state ‘–’ becomes essentially delocalized and at distances  $x \ll a$  the problem reduces to a three-body problem with two heavy fermions and one light fermion in the state ‘+’. As has been mentioned, this problem is characterized by a critical mass ratio  $\approx 13.6$  above which the behaviour of the system drastically changes. For our four-body problem this means that the effective potential at these distances becomes attractive and can support bound states. For an overcritical mass ratio, we also expect a resonance dependence of molecule–molecule collisions on the scattering length or short-range parameters of the system.

Finally, it is worth noting that for a very large  $M/m$  these resonances should be very narrow, since the repulsive effective potential at  $x > a$  is very strong. Therefore, the molecule–molecule scattering length should (on average) increase logarithmically with  $M/m$ . Obviously, the effective repulsive barrier is important for the analysis of the inelastic losses in the molecular gas. We discuss this question in more detail in section 6.

## 5. Suppressed collisional relaxation

The most exciting physics with weakly bound bosonic molecules of fermionic atoms is related to their collisional stability. Actually, these are molecules in the highest rovibrational state and they undergo relaxation into deeply bound states in molecule–molecule (or molecule–atom) collisions. The released binding energy of a deep state is  $\sim \hbar^2/2\mu R_e^2$ . It is transformed into the kinetic energy of particles in the outgoing collisional channel and they escape from the sample. Thus, collisional relaxation determines the lifetime of the Bose gas of weakly bound molecules and is therefore a crucial process. Several experiments show that such molecules consisting of bosonic  $^{87}\text{Rb}$  [55, 56] and  $^{133}\text{Cs}$  atoms [57] undergo a rapid collisional decay. On the other hand, first observations of weakly bound molecules  $\text{Li}_2$  and  $\text{K}_2$ , consisting of fermionic atoms [9, 10, 46, 12], showed that they are long-lived at densities  $\sim 10^{13} \text{ cm}^{-3}$ .

We now arrive at the point where quantum statistics of composite bosons comes into play for weakly bound molecules of fermionic atoms. First, we discuss the case of  $M/m \sim 1$ , where the interaction between molecules is characterized by a soft-core repulsion. Clearly behaving themselves as point-like bosons at large intermolecular distances, these molecules ‘start remembering’ that they consist of fermions when the intermolecular separation becomes smaller than the molecule size ( $\sim a$ ). As was explained in [43, 44], the key reason for the remarkable collisional stability of such weakly bound molecules of fermionic atoms is Fermi statistics for the atoms in combination with a large size of the molecular state (small momenta of bound fermionic atoms). The physical picture is the following. The binding energy of the molecules is  $\varepsilon_0 = \hbar^2/2\mu a^2$  and their size is close to  $a$ . The size of deep bound states is of the order of the characteristic radius of interaction  $R_e \ll a$ . 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.

The inequality  $a \gg R_e$  allows one to obtain the dependence of the molecule–molecule wavefunctions at short interparticle distances on the two-body scattering length  $a$  and thus to establish a dependence of the relaxation rate on  $a$ . In [43, 44] we have done this for  $m = M$

and found a strong decrease of relaxation with increasing  $a$ . Here we generalize these findings to the case of  $m \neq M$ , assuming that the mass ratio  $M/m$  is smaller than the critical value 13.6 and short-range physics does not influence the  $a$ -dependence of the relaxation rate.

The relaxation is essentially a three-body process which occurs when three fermions approach each other to a short distance of the order of  $R_e$ . The fourth particle does not participate in the sense 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 and also for any hyperradius of the three-fermion system  $\rho \ll a$ , the four-body wavefunction decomposes into a product:

$$\Psi = \eta(\mathbf{z})\Psi^{(3)}(\rho, \Omega), \quad (23)$$

where  $\Psi^{(3)}$  is the wavefunction of the three-fermion system,  $\Omega$  is the set of hyperangles for these fermions,  $\mathbf{z}$  is the distance between their centre of mass and the fourth atom and the function  $\eta(\mathbf{z})$  describes the motion of this atom. This function is normalized to unity and averaging over the motion of the fourth atom we see that the probability of relaxation is determined solely by the short-range behaviour of the function  $\Psi^{(3)}(\rho, \Omega)$ .

In the case of fermionic atoms with different masses one has two possible choices of a three-body subsystem out of four fermions. The most important is the relaxation in the system of one atom with the mass  $m$  and two heavier atoms with masses  $M$ .

The function  $\Psi^{(3)}$  for  $\rho \ll a$  follows from the three-body Schrödinger equation with zero total energy and, hence, can be written as  $\Psi^{(3)} = A(a)\psi(\rho, \Omega)$ , where the function  $\psi$  is independent of  $a$ . Assuming that the inelastic amplitude of relaxation is much smaller than the amplitude of elastic scattering, the dependence of the relaxation rate constant on  $a$  is related only to the  $a$ -dependence of the function  $\Psi^{(3)}$  and, hence, is given by

$$\alpha_{\text{rel}} \propto |A(a)|^2. \quad (24)$$

For finding  $\alpha_{\text{rel}}(a)$  it is sufficient to consider distances where  $R_e \ll \rho \ll a$ . At these distances we have  $\psi = \Phi(\Omega)\rho^{\nu-1}$  [44], and the function  $\Psi^{(3)}$  becomes

$$\Psi^{(3)} = A(a)\Phi(\Omega)\rho^{\nu-1}. \quad (25)$$

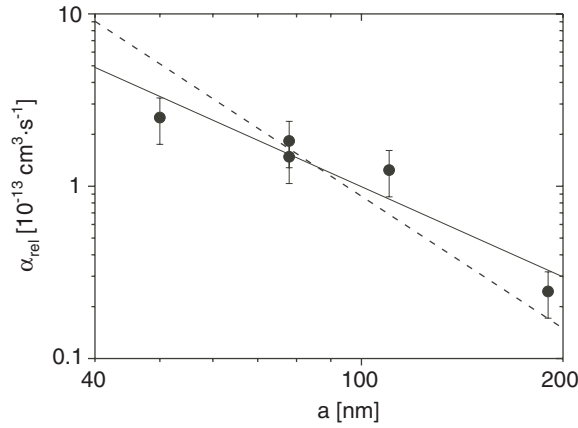
The prefactor  $A(a)$  can be found from the solution of the four-body problem in the zero-range approximation.

Quite elegantly, the  $a$ -dependence of  $A(a)$  can be determined from the following scaling considerations. The scattering length  $a$  is the only length scale in our problem and we can measure all distances in units of  $a$ . For example, rescaling  $\rho = a\rho'$  and  $\mathbf{z} = a\mathbf{z}'$ , taking into account that  $\eta(\mathbf{z})$  is normalized to unity, and using  $\Psi^{(3)}$  from equation (25) we obtain that the  $a$ -dependent coefficient in equation (23) equals  $A(a)a^{\nu-5/2}$ . By applying the same rescaling to equation (12) with the account of equation (13) we see that the same coefficient should be proportional to  $a^{-3}$ . Therefore,  $A(a) \propto a^{-\nu-1/2}$  and  $\alpha_{\text{rel}} \propto a^{-s}$ , where  $s = 2\nu + 1$ .

The exponent  $s$  depends on the mass ratio and on the symmetry of the three-body wavefunction  $\Psi^{(3)}$ . The leading relaxation channel at large  $a$  corresponds to the smallest  $\nu$ . The analysis of the three-body wavefunctions for the s-wave and p-wave atom–molecule collisions has been performed in [49]. The p-wave symmetry in the system of one light and two heavy fermions provides the smallest value of  $\nu$  which in the interval  $-1 \leq \nu < 2$  is given by the root of the function [49]

$$\lambda(\nu) = \frac{\nu(\nu+2)}{\nu+1} \cot \frac{\pi\nu}{2} + \frac{\nu \sin \gamma \cos(\nu\gamma + \gamma) - \sin(\nu\gamma)}{(\nu+1) \sin^2 \gamma \cos \gamma \sin(\pi\nu/2)}, \quad (26)$$

where  $\gamma = \arcsin[M/(M+m)]$ . For equal masses we recover  $s = 2\nu + 1 \approx 2.55$  obtained in [43, 44], and it slowly decreases with the increasing mass ratio (see section 6).



**Figure 4.** Two-body decay rate  $\alpha_{\text{rel}}$  of a  ${}^6\text{Li}_2$  molecular condensate as a function of interatomic scattering length near the  ${}^6\text{Li}$  Feshbach resonance at 834 G. Solid line: least-square fit,  $\alpha_{\text{rel}} \propto a^{-1.9 \pm 0.8}$ . Dashed line, theory:  $\alpha_{\text{rel}} \propto a^{-2.55}$ . The theoretical relaxation rate has been normalized to the experimental value at  $a = 78$  nm.

The absolute value of the relaxation rate constant is determined by the behaviour of the three-body system at short interatomic distances. Assuming that the short-range physics is characterized by the length scale  $R_e$  and the energy scale  $\hbar^2/mR_e^2$ , we can restore the dimensions and write

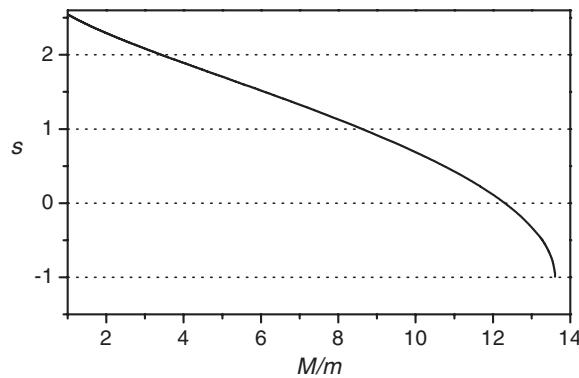
$$\alpha_{\text{rel}} = C(\hbar R_e/m)(R_e/a)^s, \quad (27)$$

where the coefficient  $C$  depends on a particular system.

Experimental studies of bosonic molecules produced in a Fermi gas by using wide Feshbach resonances at JILA, Innsbruck, MIT and ENS are well described within the presented theoretical approach. The JILA [11–13], Innsbruck [10, 14, 15], MIT [16, 17], ENS [9, 18] and Rice [19] results show a remarkable collisional stability of weakly bound molecules  $\text{K}_2$  and  $\text{Li}_2$  consisting of two fermionic atoms. 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 equation (27), is consistent with experimental data. The potassium experiment at JILA [11] and lithium experiment at ENS [18] give the relaxation rate constant  $\alpha_{\text{dd}} \propto a^{-s}$ , with  $s \approx 2.3$  for  $\text{K}_2$ , and  $s \approx 1.9$  for  $\text{Li}_2$ , in agreement with our theory ( $s \approx 2.55$ ) within experimental uncertainty. The experimental and theoretical results for lithium are shown in figure 4. The absolute value of the rate constant for a  ${}^6\text{Li}_2$  condensate is  $\alpha_{\text{dd}} \approx 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  for the scattering length  $a \approx 110$  nm. For  $\text{K}_2$  it is by an order of magnitude higher at the same value of  $a$  [11], which can be a consequence of a larger value of the characteristic radius of interaction  $R_e$ .

## 6. Collisional relaxation of molecules of heavy and light fermions

The analysis in the previous section also holds for collisional relaxation of weakly bound molecules of heavy and light fermionic atoms ( $M/m \gg 1$ ). The most efficient is again the relaxation process in which one light and two heavy fermions approach each other to distances  $\sim R_e$ , and the fourth (light) atom is separated from this three-body system by a large distance  $\sim a$ .



**Figure 5.** The dependence of the exponent  $s = 2\nu + 1$  in equation (27) on the mass ratio  $M/m$ .

However, for a large mass ratio the behaviour of the three-body system of one light and two heavy atoms changes, and the physical picture of the relaxation process is drastically modified. When the heavy atoms are separated from each other by a distance  $x \ll a$ , the light atom mediates an effective  $1/x^2$  attraction between them. This follows from the Efimov picture of effective interaction in a three-body system [48] and can be illustrated in the Born–Oppenheimer approximation, relying on the results in section 4 [54]. For  $x \ll a$ , the light atom is in the bound state ‘+’ with two heavy atoms, and from equations (18), (19) we then obtain an effective potential  $U_{\text{eff}} = \varepsilon_+ \approx -0.16\hbar^2/mx^2$ . This attraction competes with the Pauli principle which in terms of effective interaction manifests itself in the centrifugal  $1/x^2$  repulsion between the heavy atoms. The presence of this repulsion is clearly seen from the fact that in the state ‘+’ the permutation of the heavy fermions does not change the sign of the light-atom wavefunction  $\psi_{\mathbf{x},+}(\mathbf{y})$  given by equation (17). Hence, the total wavefunction of the three-body system  $\psi_{\mathbf{x},+}(\mathbf{y})\chi(\mathbf{x})$  is antisymmetric with respect to this permutation only if the wavefunction of the relative motion of heavy atoms  $\chi(\mathbf{x})$  changes its sign. Therefore,  $\chi(\mathbf{x})$  contains partial waves with odd angular momenta, and for the lowest angular momentum (p-wave) the centrifugal barrier is  $U_c(x) = 2\hbar^2/Mx^2$ . For comparable masses it is significantly stronger than  $U_{\text{eff}}(x)$ . Thus, we have the physical picture of the previous section: the Pauli principle (centrifugal barrier) reduces the probability for the atoms to be at short distances and, as a consequence, the relaxation rate decreases with the increasing atom–atom scattering length  $a$ .

The role of the effective attraction increases with  $M/m$ . As a result, the decrease of the relaxation rate with increasing  $a$  becomes weaker. In figure 5 we present the dependence of the exponent  $s$  in equation (27) on the mass ratio, obtained from equation (26) which follows from the exact solution of the three-body problem. The exponent  $s$  continuously decreases with increasing  $M/m$  and becomes zero for  $M/m = 12.33$ . In the Born–Oppenheimer picture this means that at this point one has a balance between the mediated attraction and the centrifugal repulsion.

A further increase in  $M/m$  makes  $s$  negative and it reaches the limiting value  $s = -1$  for the critical mass ratio  $M/m = 13.6$ . Thus, in the range  $12.33 < M/m < 13.6$  the relaxation rate increases with  $a$ .

For an overcritical mass ratio  $M/m > 13.6$ , we have a well-known phenomenon of the fall of a particle to the centre in an attractive  $1/x^2$  potential [29]. As has been mentioned in section 3, in this case the shape of the wavefunction at distances of the order of  $R_e$  can significantly influence the large-scale behaviour and a short-range three-body parameter is required to describe the system.

The fact that for  $M/m > 12.33$  the relaxation rate is not decreasing with an increase in the atom–atom scattering length  $a$  does not mean that the relaxation is not reduced compared to the case of molecules of bosonic atoms with the same mass ratio. For a large  $M/m$ , at distances  $x$  larger than  $a$ , the molecules interact via a strong repulsive potential  $U_{\text{eff}}(x)$  given by equation (22). Away from possible resonances in molecule–molecule collisions, this barrier reduces the amplitude of the wavefunction at intermolecular distances  $\sim a$  and, hence, leads to a suppression of the relaxation rate. Estimating the corresponding tunnelling probability  $P$  in the WKB approach, we obtain  $P \propto \exp(-B\sqrt{M/m})$  where  $B \approx 0.6$ .

We thus see that one also expects the suppression of collisional relaxation for weakly bound molecules of light and heavy fermionic atoms. However, the suppression factor is independent of the atom–atom scattering length  $a$  and is governed by the mass ratio  $M/m$ . The mechanism of this suppression originates from Fermi statistics for the light atoms, which leads to a strong repulsion between molecules at large intermolecular distances. This result should have implications for experiments on the formation of molecules in mixtures of  ${}^6\text{Li}$  with much heavier fermionic atoms, for example  ${}^{87}\text{Sr}$  ( $M/m \approx 14.5$ ) or  ${}^{173}\text{Yb}$  ( $M/m \approx 29$ ).

It is worth noting that one also expects collisional stability of a mixture of light and heavy fermionic atoms on the BCS side of a Feshbach resonance ( $a < 0$  and  $k_{\text{F}}|a| \ll 1$ ). Three-body recombination to deeply bound states will be suppressed as  $(k_{\text{F}}|a|)^2$  compared to the case of bosonic atoms with the same densities, masses and scattering length. The stability of a mixture of light and heavy fermionic atoms in the strongly interacting regime requires a separate investigation.

## 7. Molecular BEC and prospects for manipulations with weakly bound molecules

The suppression of the relaxation decay rate of weakly bound molecules of fermionic atoms has a crucial consequence for the physics of these molecules. At realistic temperatures, the relaxation rate constant  $\alpha_{\text{dd}}$  is much smaller than the rate constant of elastic collisions  $8\pi a_{\text{dd}}^2 v_T$ , where  $v_T$  is the thermal velocity. For example, for  $\text{Li}_2$  weakly bound molecules at a temperature  $T \sim 3 \mu\text{K}$  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 molecules and cooling the Bose-condensed gas to temperatures of the order of its chemical potential. Long-lived BEC of weakly bound molecules has been recently observed for  ${}^{40}\text{K}_2$  at JILA [12, 13] and for  ${}^6\text{Li}_2$  at Innsbruck [14, 15], MIT [16, 17], ENS [18] and Rice [19]. Measurements of the molecule–molecule scattering length confirm the result  $a_{\text{dd}} = 0.6a$  with accuracy up to 30% [15, 18]. This result is also confirmed by recent Monte Carlo calculations [58] of the ground state energy in the molecular BEC regime.

Remarkable achievements in the physics of ultracold Fermi gases attract a lot of attention and draw fascinating prospects for future studies. The prospects are to a large extent related to the very long lifetime of weakly bound bosonic molecules of fermionic atoms, which allows interesting manipulations with these molecules. Arranging a deep evaporative cooling of their Bose-condensed gas to temperatures of the order of the chemical potential, one can then convert the molecular BEC into fermionic atoms by adiabatically changing the scattering length to negative values. This provides an additional cooling, and the obtained atomic Fermi gas will have extremely low temperatures  $T \sim 10^{-2}T_{\text{F}}$ , where  $T_{\text{F}}$  is the Fermi temperature. The gas can then enter the superfluid BCS regime [59]. Moreover, at such temperatures one has a very strong Pauli blocking of elastic collisions and expects the collisionless regime for the thermal cloud. This is promising for identifying the BCS-paired state through the observation of collective oscillations or free expansion [60, 61, 18, 15, 62].

Recent experiments at Innsbruck, ENS, JILA and MIT have explored the BEC–BCS crossover regime and shown a remarkably reversible behaviour of the gas from the BEC region to the BCS region and back over the duration of seconds [14, 18, 13, 17, 63]. Experiments have also measured the pairing gap in the crossover region using RF spectroscopy [64]. The energy gap varies between the binding energy of the molecules in the region  $a > 0$ , and a density-dependent (and much smaller) value in the region  $a < 0$  where no stable two-body bound state exists. Further experiments at JILA and MIT have proven that fermionic atom pairs present in the strongly correlated regime at  $a < 0$  behave as Bose-condensed pairs [13, 17, 63]. For revealing the nature of this superfluid pairing it is promising to make experiments with rotating Fermi gases [65] in the strongly interacting regime, where one expects the formation of vortices and vortex lattices [66, 67]. Another idea is to look directly at a signature of the long-range order in the superfluid phase by an interference experiment as suggested in [68].

It will also be interesting to transfer the weakly bound molecules of fermionic atoms to their ground ro-vibrational state by using two-photon spectroscopy, as has been done in [69, 70] for molecules of bosonic atoms. Long lifetime of weakly bound molecules 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 molecules of bosonic atoms, where one has severe limitations on achievable densities and lifetimes. One can then extensively study the physics of molecular Bose–Einstein condensation. Moreover, heteronuclear molecules which are supposed to be formed in mixtures of different fermionic atoms can be polarized by an electric field. One then gets a gas of dipoles interacting via anisotropic long-range forces, which drastically changes the physics of Bose–Einstein condensation [71].

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