A composite-boson approach to molecular Bose-Einstein condensates in mixtures of ultracold Fermi gases

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(Dated: October 5, 2016)

We show that an Ansatz based on independent composite bosons [Phys. Rep. 463, 215-320 (2008)] accurately describes the condensate fraction of molecular Bose-Einstein condensates in ultracold Fermi gases. The entanglement between the fermionic constituents of a single Feshbach molecule then governs the many-particle statistics of the condensate, from the limit of strong interaction to close to unitarity. This result strengthens the role of entanglement as the indispensable driver of composite-boson-behavior. The condensate fraction of fermion pairs at zero temperature that we compute matches excellently previous results obtained by means of fixed-node diffusion Monte Carlo methods and the Bogoliubov depletion approximation. This paves the way towards the exploration of the BEC-BCS crossover physics in mixtures of cold Fermi gases as well as the implementation of Hong-Ou-Mandel-like interference experiments proposed within coboson theory.

PACS numbers: 05.30.Fk, 67.85.Lm, 03.75.Hh, 03.75.Gg.

The experimental achievement of Bose-Einstein condensates (BEC) [1–3] has opened a new and exciting era in the field of atomic and molecular physics [4–6]. This phenomenon is a consequence of the characteristic many-particle statistics of bosons, which is reflected by the commutation relations of their respective creation and annihilation operators. Atoms and molecules, however, are ultimately made of fermions, which, with a sufficiently strong attractive interaction, can be bounded to form structureless bosons. Feshbach resonances in mixtures of cold Fermi gases have provided a procedure to control the interaction between fermions of different species, and, thus, a way to observe the formation of BECs of molecules [4–6, 7–11] as well as the BEC-BCS (superfluidity) crossover [10, 11, 13]. The many-particle statistics are governed by the interaction between fermions, e.g., the fraction of fermion pairs that condense decreases with the magnetic field across Feshbach resonance, from the limit of strong attractive interaction (BEC) to the repulsive interaction regime (BCS) [10, 11]. This many-interacting-particle-problem constitutes a theoretical challenge that has been addressed with mean field theories [14]. These approaches, however, overestimate the momentum distribution of the Fermi gas and consequently the condensate fraction. To describe the BEC-BCS crossover theoretically, one has to resort to Monte Carlo simulations [15]. In the strong-interaction regime, the collective statistics of molecular BEC can be well approximated by the Bogoliubov quantum depletion theory [16].

In the theory of cobosons (composite bosons) [17], the wavefunction of a fermion pair |Ψ⟩ is represented in second quantization by application of the creation operator $\hat{c}^\dagger$ of the two-fermion composite on the vacuum, |Ψ⟩ = $\hat{c}^\dagger |0\rangle$, and the successive application of this operator defines a Fock state of $N$ identical fermion pairs

$$|N\rangle = \frac{(\hat{c}^\dagger)^N}{\sqrt{N!\chi_N}} |0\rangle . \tag{1}$$

The normalization factor $\chi_N$ [18] reflects how, in accordance with the Pauli principle, the fermion pairs must distribute themselves over the available single-fermion states associated to the internal degrees of freedom of the state |Ψ⟩. In this description, the interaction between fermion pairs can only come from fermion exchanges [19]: in other words, the physics of the many-particle system emerges from the state |Ψ⟩ together with the fermion exchange interaction among the $N$ fermion pairs [20], and both ingredients are reflected in $\chi_N$. Despite the fact that Bose-Einstein condensates (i.e. Fock states) of atoms and molecules constitute immediate candidates for an application of the coboson framework, this connection has received little attention; For Gaussian states, the condensate fraction was calculated at finite temperature [21], the stability of a Bose-Einstein condensate has been revisited [22], and a general formalism for composite bosons was developed in Ref. [23] at finite temperature and in Ref. [19] for attractively interacting fermion pairs at zero temperature. On the other hand, coboson theory has been extensively applied to phenomena such as excitons and Cooper-pairing [24]. Nevertheless, the determination of a physical system with experimentally accessible nontrivial compositeness effects remained a challenge. Here, we take a step forward in this sense and show that the finite condensate fraction of fermion pairs in experiments of ultracold interacting Fermi gases is a compositeness effect accurately described by this theory.

We start completely from scratch in a reductionistic manner, and establish the state |Ψ⟩ that describes two bound fermion on the side of a Feshbach resonance where the scattering length is positive. With that state
in hand, we study the emergent many-particle statistics of molecular Bose-Einstein condensates. By using tools borrowed from quantum information [25] and a discretization method to decompose the state \( |\Psi\rangle \) describing the fermion pair in the Schmidt form [3], we compute the entanglement between the compounds of the molecule, and the closely related normalization ratio \( \chi_{N+1}/\chi_N \), which governs the particle statistics of \( N \) fermion pairs in the state \( |N\rangle \). In particular, we show that the normalization ratio exhibits a universal behavior with the parameter \( 1/(k_F a) \), which can be understood as the ratio between interparticle spacing and the scattering length \( a \), and which fixes the energy scale of the system \( (k_F = (6\pi^2 n)^{1/3}) \) is the Fermi wave number of a non-interacting gas with atom-pair density \( n = N/V \)). This universality allows us to fully characterize the statistics of the system by the entanglement between the molecular constituents. We also obtain the condensate fraction of fermion pairs and compare our results to Bogoliubov quantum depletion and fixed-node diffusion Monte Carlo simulations (FN DMC) [15]. Our results match the established approaches remarkably well in the strong-interaction regime, and deviate slightly near unitarity. This deviation is due to the strong-binding approximation that we use on the wavefunction. However, the finite condensate fraction at unitarity predicted by coboson theory [19] indicates that this simple model reproduces essential physics of the BEC-BCS crossover.

As a test, we apply the model of Feshbach molecule of Refs. [1] to the \(^6\text{Li}_2\) broad resonance in order to compute the molecular ground state \( |\Psi\rangle \). It consists of two coupled channels, namely an open channel \( \theta \) (background or entrance channel) and a closed channel \( \epsilon \). In Feshbach magneto resonances, these channels can be identified as two different hyperfine or spin states of the constituent fermionic atoms of a molecule, which couple via Coulomb or exchange interactions [6]. The Hamiltonian of two interacting atoms of mass \( m \) in an harmonic trap is given by

\[
H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{m\omega^2}{2} (r_1^2 + r_2^2) + \hat{V}_{\text{int}}(\vec{r}_1 - \vec{r}_2),
\]

where \( \omega \) is the trapping frequency and \( \hat{V}_{\text{int}} \) the potential energy of the atom-atom interaction. Using the center-of-mass \( \vec{R} = (\vec{r}_1 + \vec{r}_2)/2 \) and relative \( \vec{r} = \vec{r}_1 - \vec{r}_2 \) coordinates, the Hamiltonian factorizes as \( H = H_R + H_r \) and the state of the system is separable in such coordinates: \( |\Psi\rangle = |\psi_R\rangle |\psi_r\rangle \). The ground-state solution of the center-of-mass Schrödinger equation \( H_R |\psi_R\rangle = E_R |\psi_R\rangle \) is given by the isotropic harmonic oscillator energy \( E_R = \hbar \omega/2 \) and the Gaussian function \( \psi_R(R) = (\pi^{-1/4}e^{-R^2/2\sigma^2})^3 \), where \( \sigma = \sqrt{2\hbar/m\omega} \) is the radius that characterizes the size of the spherical trap such that 95% of the wave function \( \psi_R(R) \) is confined in the volume \( V = (4/3)\pi(2\sigma)^3 \).

The interaction between atoms is described by a spherical well potential \( \hat{V}_{\text{int}}(r) \) with a finite range for the interaction \( r_0 \); within the range of interaction, \( r = |r| < r_0 \), the attractive potential of the closed (open) channel is given by \(-V_c\) \((+V_c)\), and outside the interaction range by \( \infty \). The two atoms collide at energy \( E_c = -E_m \) and couple to a molecular bound state with effective binding energy \( E_m \). Experimentally, an external magnetic field \( B \) induces a Zeeman shift in the energy level of both channels, such that \( E_m \) and, consequently, the effective strength of the atom-atom interaction can be tuned with \( B \). To solve analytically the relative coordinate equation \( H_r |\psi_r\rangle = E_r |\psi_r\rangle \) of this two-particle system, we assume that the binding energy is larger than the confining energy \( 2E_m > \hbar\omega/2 \). This approximation in the energy scale \( 2E_m > \hbar\omega \) is equivalent to \( a < 2\sigma \) in the length scale. Experiments with Bose-Einstein condensates of Feshbach molecules are characterized by trapping frequencies \( \omega \) of the order of \((2\pi)10^2\text{-}10^4 \) Hz [8, 9, 29]. In this frequency range the binding energy fulfills \( 2E_m > \hbar\omega \) for a wide range of the magnetic field \( B \), which extends to the BEC-BCS crossover region \((k_F a > 1)\), where \( k_F a = (16/9\pi)^{-1/3}(\hbar/2m)^{1/2}\sigma/\sqrt{\omega} \) for a single fermion pair \( N = 1 \), see Fig. 1. The details of the eigenenergy \(-E_m\) equation and the eigenstate \( |\psi_r\rangle = \psi_o(r) |o\rangle + \psi_c(r) |c\rangle \) of the relative coordinate are provided in the supplemental material [20], together with further details about the two-state model for the \(^6\text{Li}_2\) molecule and the approximations that we use.

The hyperfine or spin-spin interactions in cold atom systems, i.e., the coupling between open and closed channel, are typically many orders of magnitude weaker than inner-channel interactions (or any short-range exchange potential). In this regime, the scattering length, which

![FIG. 1: Binding energy as a function of the magnetic field \( B \) (solid line). Horizontal lines are the confining energies \( E_{\text{h.o.}}/2 \) for the frequencies \( \omega = 2\pi \cdot 10^2 \) Hz (dashed), \( 3 \cdot 2\pi \cdot 10^3 \) Hz (dotted dashed) and \( 2\pi \cdot 10^5 \) Hz (dotted). For these trapping frequencies, the BEC-BCS crossover extends to the strong-binding regime (\( E_m > E_{\text{h.o.}}/2 \)), i.e., from the vertical lines given by \( k_F a = 1 \) with \( N = 1 \) to the right, as the arrows indicate. The unitary limit is found in the resonant position \( B_{\text{res}} \) (vertical solid line).](image-url)
is reciprocal to the strength of the interaction, can be approximated by

$$\frac{a - r_0}{a_{bg} - r_0} = 1 + \frac{\Delta B}{B - B_{res}},$$  \hspace{1cm} (3) \]

where $\Delta B$ and $B_{res}$ are the resonance width and the resonance position, respectively, and $a_{bg}$ is the scattering background. Although the actual $^6\text{Li}_2$ Feshbach resonance has more than one closed channel and the potential energies of both closed ($V_c$) and open ($V_o$) channels, are certainly not well potentials \cite{Nord}, the simple model that we use reproduces essential physics of Feshbach resonances such as the binding energy or the channel mixing fraction \cite{Itz}.

While every two-particle wavefunction admits a Schmidt decomposition, it is difficult – if not impossible – to find a close analytical solution for such a decomposition for wavefunctions in continuous variables beyond the paradigmatic system of coupled oscillators \cite{Klein}. Hence, we resort to the discretization method introduced in Ref.\cite{Klein}, which exploits the cylindrical symmetry of a two-particle-systems by means of a Legendre expansion of the wavefunction. With this technique, the molecular wavefunction $|\Psi\rangle$ can be approximated by a Schmidt expansion \cite{Klein}

$$|\Psi\rangle = \sum_j S_j \sqrt{\lambda_j^{(1)}} (r_1^{(1)})(r_2^{(1)}) |a\rangle +$$

$$+ \sum_j S_j \sqrt{\lambda_j^{(c,1)}} (r_1^{(c,1)})(r_2^{(c,1)}) |c\rangle,$$  \hspace{1cm} (4) \]

with finite Schmidt rank $S$. The Schmidt coefficients fulfill $0 < \lambda_j^{(c,c,1)} < 1$, and $\phi_j^{(a,c,1)}$ are the corresponding single-fermion states (normalized to unity) of atoms 1 and 2, in the open and closed channel, respectively. The Schmidt rank $S = (2l + 1)\cdot (n_{max} + 1)\cdot (l_{max} + 1)$ is given by the number of coefficients $\lambda_j = \lambda_{nl}$ associated to the principal $n$ and angular momentum $l$ quantum numbers (with degeneracy $2l + 1$) of the molecular state $|\Psi\rangle$ \cite{Klein}. The closed channel contribution to the wave function ($\sum_j S_j \lambda_j^{(c,1)}$) is only relevant, however, in the weak-interaction region $(k_Fa)^{-1} \ll 1$, near the resonant position. Therefore, it is sufficient to compute the open-channel Schmidt distribution to obtain a minimal accuracy in the state normalization of $|\langle \Psi | \Psi \rangle| \approx \sum_j S_j \lambda_j^{(c,1)} > 0.996$, up to the value $(k_Fa)^{-1} \approx 0.19$, with $n_{max} = 350$ and $l_{max} = 79$. We will omit the index “$c$” in the open channel distribution $\lambda_j = \lambda_j^{(c,1)}$, which is the Schmidt coefficient distribution that characterizes the state $|\Psi\rangle$ hereafter.

With the above discretization method applied to the wavefunction $|\Psi\rangle$, we are able to quantify the entanglement between the fermionic atoms, along the positive scattering length region of the Feshbach resonance, e.g., by means of $E = 1 - P$, the linear entropy, where $P = \sum_j S_j \lambda_j^{(c,1)}$ is the purity of the single-fermion reduced density matrix. The entanglement of a single Feshbach molecule ($N = 1$) depends only on the parameter $(16/\pi)^{1/3} \sigma/a = (k_Fa)^{-1}$, since the Hamiltonian \cite{Itz} can be rescaled by the trapping frequency and written in terms of the ratio between the atom-atom interaction strength and $\omega^2$. When the magnetic field is ramped up the scattering length of the $^6\text{Li}_2$ Feshbach resonance increases. Consequently, the binding energy and entanglement decrease as shown in Fig.2. In the BEC regime, the fermion pair is maximally entangled for $k_Fa \ll 1$, and this entanglement is significantly decreasing up to the BEC-BCS crossover border ($k_Fa = 1$). In the crossover region, the entanglement decreases drastically to a finite value ($E_{min} \approx 0.47$, see inset panel of Fig.2) in the limit of weak binding ($k_Fa \gg 1$).

We now turn to a many-body description of molecular Bose-Einstein condensates using coboson theory. The wavefunction \cite{Itz}, which describes the fermion pairs in the molecular ground state $|\Psi\rangle$, has naturally motivated the introduction of composite boson creation operator \cite{Itz}

$$\hat{c}^\dagger = \sum_j \sqrt{\lambda_j} \hat{a}_j^{\dagger} \hat{b}_j^{\dagger},$$

where $\hat{a}^{\dagger}_j$ ($\hat{b}^{\dagger}_j$) creates a fermion $1$ ($2$) in the Schmidt mode $\phi_j^{(1)}$ ($\phi_j^{(2)}$). Thus, the action of the operator $\hat{c}^\dagger$ on the vacuum describes the ground state of a Feshbach molecule $|\Psi\rangle = \hat{c}^\dagger |0\rangle$. The $N$-fermion-pair Fock state \cite{Itz},

$$|N\rangle = \frac{1}{\sqrt{N!X_N}} \sum_{j_1 \neq j_2 \neq \cdots \neq j_N}^1 \prod_{k=1}^N \sqrt{\lambda_{j_k}} \hat{a}^{\dagger}_{j_k} \hat{b}^{\dagger}_{j_k} |0\rangle,$$  \hspace{1cm} (5) \]

![FIG. 2: Entanglement between the atoms comprising a Feshbach molecule (red dots, solid line guides the eye) as a function of the dimensionless parameter $(16/\pi)^{1/3} \sigma/a = (k_Fa)^{-1}$ with $N = 1$. The shaded area depicts the strong-binding region $2Em > E_{h.o.}$ which is bounded by the vertical dotted line $2Em = E_{h.o.}$. The insets show the Schmidt coefficient distributions $\lambda_j = \lambda_{nl}$ of the state $|\Psi\rangle$ for $(k_Fa)^{-1} = 3$ and $0.5$ (dots indicated by the arrows). The upper panel shows the finite entanglement in the limit of weak binding $k_Fa \gg 1$.](image-url)
then describes a Bose-Einstein condensate of molecules, where the composite boson normalization factor is given by the elementary symmetric polynomial

$$\chi_N = N! \sum_{p_1 < p_2 < \ldots < p_N} \lambda_{p_1} \lambda_{p_2} \cdots \lambda_{p_N}. $$

The available recursive formula for the normalization factor facilitates its computation for large number of Schmidt coefficients.

As a consequence of the Pauli exclusion principle, the application of the creation operator $c^\dagger$ on the $N$-coboson-state yields a sub-normalized state

$$c^\dagger |N\rangle = \sqrt{\frac{\chi_{N+1}}{\chi_N}} \sqrt{N+1} |N+1\rangle. \quad (6)$$

When a fermion pair in the state $|\Psi\rangle$ is added to the state $|N\rangle$, the fermion pair is accommodated among the $S-N$ unoccupied Schmidt modes, which only occurs with probability $\sum_{i \notin \{j_1, \ldots, j_N\}} \lambda_i$, see Eq. (5). Therefore, the probability to successfully add a coboson to the state $|N\rangle$ is given by sum over the possible configurations of the set $j_1, \ldots, j_N$

$$\frac{1}{\chi_N} \sum_{1 \leq j_m \leq N} \prod_{k=1}^{S} \lambda_{j_k} \sum_{i \notin \{j_1, \ldots, j_N\}} \lambda_i = \frac{\chi_{N+1}}{\chi_N}, \quad (7)$$

i.e., by the normalization ratio $\chi_{N+1}/\chi_N$. Fermion pairs in the state $|N\rangle$ are correlated among themselves due to the Pauli principle. Hence, despite the molecular BEC being created by the $N$ successive addition of identical fermion pairs in the molecular ground state $|\Psi\rangle$, and the resulting state $|N\rangle$ constitutes the ground state of the $N$ fermion-pairs [19], there is no guarantee to find each of the $N$ fermion pairs in the state $|\Psi\rangle$, that is, $|N\rangle \not \equiv |\Psi\rangle^\otimes N$.

Indeed, the effective fraction of fermion pairs that populate the single-molecule ground state $|\Psi\rangle$ is given by the expectation value [21]

$$\langle N| c^\dagger c |N\rangle / N = \frac{1}{N} + \left(1 - \frac{1}{N}\right) \frac{\chi_{N+1}}{\chi_N} \leq 1. \quad (8)$$

The above expectation value constitutes, in fact, the condensate fraction of pairs at temperature $T = 0$. This non-ideal bosonic condensation results from the competition of the constituent fermions to occupy the single-fermion states, or Schmidt modes, of $|\Psi\rangle$, and such competition increases with $a$ (see the Schmidt coefficients distributions of the insets in Fig. 2). In Fig. 3 we show the effective fermion pair condensation across the positive scattering length resonance $\alpha > 0$, for $N = 33$. The condensate fraction matches previous results obtained by FN DMC [15], and by the Bogoliubov quantum depletion approximation for a condensate of composite bosons $\alpha = 1 - 8 \sqrt{m_{cd}/(3 \sqrt{\pi})}$, where $a_{dd} = 0.6a$ is the characteristic dimer-dimer scattering length. In the weak binding region, due to our wavefunction approximation [20], the condensate fraction undermatches the FN DMC result. Nevertheless, our approach predicts finite entanglement in the limit of weak interaction [19], which leads to a finite condensate fraction at unitarity, $1/(k_F a) = 0$. The minimum condensate fraction close to unitarity that we computed, decreases with the number of fermion pairs $N$ as $(1 + (N-1)\epsilon_{\min})/N$, in qualitative agreement with the FN DMC result [15]. In this regard, the coboson theory reaches beyond mean-field and Bogoliubov theories, which makes it a candidate for the description of the BEC-BCS crossover.

![FIG. 3: Condensate fraction predicted by coboson theory $\langle N| c^\dagger c |N\rangle / N$ as a function of the dimensionless parameter $(k_F a)^{-1}$ (red dots, solid line guides the eye) for $N = 33$. Black dots correspond to the FN DMC results [15], and the black dashed line to the Bogoliubov depletion of a Bose gas with $a_{dd} = 0.6a$. The shaded area depicts the strong-binding region and the inset shows the universality of the normalization ratio $\chi_{N+1}/\chi_N$ with $(k_F a)^{-1}$.](image)

The characteristic statistics of many-particle quantum systems, at the level of fermions and bosons, are established by the commutation relations satisfied by the respective creation and annihilation operators. Non-ideal bosonic operators $c^\dagger$, however, obey non-conventional bosonic commutation relations, such that the expectation value of the commutator $[c, c^\dagger]$ on the state $|N\rangle$ reads

$$\langle N| [c, c^\dagger] |N\rangle = 2 \frac{\chi_{N+1}}{\chi_N} - 1, \quad (9)$$

When Eq. (9) equate to unity $(\chi_{N+1}/\chi_N = 1)$ the $N$ composite bosons behaves as ideal bosons, while deviations from unity entails observable consequences induced by the statistics of the constituent fermions [19, 21, 37-41]. The normalization ratio quantifies, therefore, the bosonic quality of the $N$ fermion pair state $|N\rangle$ [32, 33], and governs the many particle statistics of the system [8]. For interacting Fermi gases, several exact universal relations (Tan relations) has been shown, valid for all temperatures and spin compositions, which do not depend on details of the interparticle interaction. The
Tan relations connect a microscopic quantity, namely, the momentum distribution of the fermions, to macroscopic observables [12]. This universality of the macroscopic observables with the dimensionless parameter \((k_F a)^{-1}\) is also reflected by the normalization ratio \(\chi_{N+1}/\chi_N\). The inset of Fig. 3 clearly shows that the normalization ratio is a function only of the parameter \(k_F a\); for a given \(k_F a\), the normalization ratio is independent of the number of fermions pairs \(N\) such that all curves (for \(N = 2, 3, 5, 10\)) collapse, as also occurs for different trapping frequencies. We numerically find that \(\chi_{N+1}/\chi_N\) evaluated at scattering length \(a\) fulfills

\[
\frac{\chi_{N+1}}{\chi_N}_{a'=a} \approx \frac{\chi_{N-m+1}}{\chi_{N-m}}_{a'=\left(\frac{N}{N+m}\right)^{1/3} a} \approx \chi_2|_{a'=N^{1/3} a}.
\]

where \(\chi_2 = \mathcal{E} = 1 - P\). This relation significantly simplifies the computation of the normalization ratio for large \(N\), which becomes computationally challenging otherwise [32, 33]. The many-particle statistics of a molecular BEC is fully characterized by the entanglement between the atoms that compose each single molecule, and can therefore be controlled magnetically via Feshbach resonance. For instance, when manipulating magnetically the scattering length \(a\) [31], the condensate fraction of a BEC of \(N\) molecules depends uniquely on the entanglement \(\mathcal{E}\) of a single molecule, evaluated at scattering length \(a' = N^{1/3} a\). This reflects the capability of coboson theory to simplify the theoretical description of interacting cold Fermi gases.

In summary, the particle statistics of Bose-Einstein condensates of bi-atomic molecules is accurately described by a model of independent composite bosons. The condensate fraction of fermion-pairs in mixtures of Fermi gases is reproduced accurately in the strong-interaction-regime at zero temperature. Within coboson theory, the state of one fermion pair completely characterizes the collective statistics of the many-identical-pair-system due to fermionic exchange interaction. Thus, the entanglement between two fermions in a single-molecule bound state controls the many-particle statistics, since it approximately reflects the ratio of fermions to available single-fermion states [31], it leads to a universality of the normalization ratio with the dimensionless parameter \(k_F a\) that characterizes the Fermi gas. Our result is valid for any species of bound fermion pairs. Because of the strong-binding approximation to the wavefunction, our theory deviates in the unitarity region, but the result of a finite value for the condensate fraction near unitarity indicates that the coboson theory is a strong candidate to explain the BEC-BCS crossover. In order to explore and demarcate the scope of coboson theory, it should be tested with more realistic wavefunctions, which could lead to an exact characterization of the BEC-BCS crossover up to unitarity, and also against observables [12] beyond the condensate fraction. Nevertheless, the present work underlines the fundamental importance of entanglement for the bosonic behavior of bound fermions. The application of analytical bounds on the normalization ratio [32, 33] will further simplify the evaluation of observables in molecular BECs.

When applied to atoms, coboson theory confirms that nucleus-electron-compounds constitute very good bosons indeed – the purity of the single-electron density-matrix of a trapped hydrogen atom is of the order of \(10^{-12}\) [31] – rendering non-trivial predictions of deviations from ideal bosonic behavior or the observation of compositeness effects in atomic BECs infeasible. From that perspective, the application of coboson theory to the BEC-BCS-crossover is remarkable, as it provides a prominent system with experimentally accessible non-trivial compositeness effects, such that coboson theory yields a clear physical explanation for the finite condensate fraction: competition of the fermionic constituents for available single-fermion states. Consequently, coboson theory constitutes a powerful tool to explore theoretically new physical phenomena, and it can be applied fearlessly to molecular BECs. As a direct application, Hong-Ou-Mandel-like experiments [43] of two interfering molecular BECs [39, 44], in which the particle statistics are controlled by manipulating the inter-particle interaction, provide a wealth of observable effects of imperfect bosonic behavior. Observables which manifest compositeness effects within coboson theory, such as second order correlation functions or the Mandel’s parameter [37], should be tested experimentally. More in general, the present work underlines how the reductionistic coboson theory provides a physical explanation to why atoms, molecules and, in general, particles which are ultimately constituted by bound fermions, behave as bosons and are able to condense.

We thank Luis D. Angulo and Tomasz Wasak for helpful comments on the numerical code and on the Feshbach model, respectively. We also thanks Rocio Jaurégui, Klaus Mølmer, Juan Omiste and Ana Majtey for stimulating discussions and the CSIRC of the University of Granada for providing the computing time in the Alhambra supercomputer. P.A.B. gratefully acknowledges support by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazilian agency) through a BJT Ciência sem Fronteiras Fellowship, and by the Spanish MINECO project FIS2014-59311-P (co-financed by FEDER). I.R. also acknowledges partial support from CNPq.

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SUPPLEMENTAL MATERIAL

In this supplemental material we provide the details of the Feshbach molecule model presented in Refs. [1,2], that we use in the main text to describe the molecular ground state \(|\Psi\rangle\). The binding energy eigenequation and the scattering length are derived in the weak coupling regime, (between the open and closed channels), and the molecular wave function is computed assuming that the inter-atomic interaction energy is larger than the energy of the confining potential. The model is applied to the \(^6\)Li\(_2\) molecule. We also provide a description of the discretization method of Ref. [3] which allows to obtain the approximate Schmidt decomposition of the molecular state.

Feshbach molecule model

Here we solve the system Hamiltonian (Eq.(2) of the main text) which describes two interacting particles in an harmonic trap

\[
H = -\frac{\hbar^2}{2m} \left( \nabla_i^2 + \nabla_j^2 \right) + \frac{m\omega^2}{2} (r_1^2 + r_2^2) + V_{\text{int}}(r_1, r_2),
\]

where \(\omega\) is the frequency trapping, \(m\) is the mass of the \(^6\)Li atom and \(V_{\text{int}}\) the potential energy of the atom-atom interaction. Using the center of mass, \(\vec{R} = (r_1 + r_2)/2\), and the relative coordinate, \(\vec{r} = r_1 - r_2\), the Hamiltonian factorizes \(H = H_R + H_0\), and the wave function of the system is separable in such coordinates \(|\Psi(r_1, r_2)\rangle = |\Psi(R)\rangle|\psi_\tau(r)\rangle\). The Schrödinger equation of the system \(H |\Psi\rangle = E_{\text{tot}} |\Psi\rangle\) reads, therefore,

\[
\left[ -\frac{\hbar^2}{2m_R} \nabla_R^2 + \frac{m_R\omega_R^2}{2} R^2 \right] |\psi_R\rangle = E_R |\psi_R\rangle, \quad (ii)
\]

\[
\left[ -\frac{\hbar^2}{2m} \nabla_\tau^2 + \frac{m\omega^2}{2} \tau^2 + V_{\text{int}}(r) \right] |\psi_\tau\rangle = E_\tau |\psi_\tau\rangle, \quad (iii)
\]

where \(E_{\text{tot}} = E_R + E_\tau\), \(m_R = 2m\) and \(m_\tau = m/2\). The ground state solution of the center of mass differential equation \(\text{(ii)}\) is given by the ground state eigenenergy of the isotropic harmonic oscillator \(E_R = E_{\text{h.o.}} = 3\hbar\omega/2\) and the Gaussian wave function

\[
|\psi_R(R)\rangle = \frac{1}{\sigma^{3/2}\pi^{3/4}} e^{-\frac{R^2}{2\sigma^2}}, \quad (iv)
\]
where \( 2\sigma = \sqrt{2\hbar/m\omega} \) characterize the size of the harmonic trap.

We solve the Schrödinger equation of the relative coordinate \((iii)\) in the strong binding regime, such that the scattering length is positive and lower than the harmonic oscillator length \(0 < a < 2\sigma\). In this limit, the relative coordinate wave function is unaffected by the harmonic trap and the second term in the left side of Eq. \((iii)\) can be neglected. Thus, the relative coordinate Schrödinger equation can be approximated by

\[
E_r |\psi_r\rangle = \frac{\hbar^2}{m} \left(-\nabla^2_r + \hat{V}_\text{int}'(r)\right) |\psi_r\rangle, \tag{v}
\]

which has analytical solution \([1]\). The fermion pair has a molecular bound state \((E_r = -E_m < 0)\) near the continuum, and the binding energy of the atoms \(E_m\), in the strong binding regime, is larger than the confining energy of the molecule \(2E_m > E_{ho}\).

The interaction potential \(\hat{V}_\text{int} = \hbar^2/m\hat{V}_\text{int}'\) of the two-state model that we use to is described a Feshbach molecule is given by a spherical well potential with a finite range for the interaction \(r_0\) \([1]\):

\[
\hat{V}_\text{int}'(r) = \begin{cases} 
-\left(\frac{q_o^2}{\Omega} \frac{\Omega}{q_o^2 - \epsilon_c - \mu B} \right) & \text{For } r < r_0 \\
0 \begin{pmatrix} 0 & 1 \\ 0 & \infty \end{pmatrix} & \text{For } r > r_0 \tag{vi}
\end{cases}
\]

where the attractive potential of the closed (open) channel is given by \(V_o = -\hbar^2q_o^2/m\) \((V_o = -\hbar^2q_o^2/m)\) and \(\Omega\) is the coupling amplitude between the closed and the open channels. The two atoms collide at energy \(E_r = -E_m = -\hbar^2\epsilon_m/m\) in the entrance (open) channel and couple to the molecular bound state supported in the closed channel with an energy \(E_c = \hbar^2\epsilon_c/m\). Experimentally, an external magnetic field \(B\) induces a Zeeman shift in the energy level of both channels, such that the energy between the continuum and the bare state can be tuned linearly with an energy given by \(-\mu B = -\hbar^2\mu_B/m\), where \(\mu = \mu_o - \mu_c\) and \(\mu_o (\mu_c)\) is the magnetic moment of the atoms in the open (closed) channel.

To solve the above coupled differential equation \([v]\) it is useful to introduce the superposition states

\[
|+\rangle = \cos \theta |\psi_o\rangle + \sin \theta |\psi_c\rangle, \quad |-\rangle = -\sin \theta |\psi_o\rangle + \cos \theta |\psi_c\rangle, \tag{vii}
\]

with \(\tan 2\theta = 2\Omega/(q_o^2 - q_c^2 + \epsilon_c + \mu B)\). The scattering length \(a\) is defined from scattering in free space with zero relative kinetic energy. Hence solving Eq. \([v]\) for \(E_r = 0\) the following scattering length equation is obtained:

\[
\frac{1}{r_0 - a} = \frac{q_+ \cos^2 \theta}{\tan q_+ r_0} + \frac{q_- \sin^2 \theta}{\tan q_- r_0}, \tag{viii}
\]

where

\[
q_+ = \sqrt{q_o^2 + q_c^2 - \epsilon_c - \mu B + (q_o^2 - q_c^2 - \epsilon_c - \mu B) \sec 2\theta} / \sqrt{2} \tag{ix}
\]

\[
q_- = \sqrt{q_o^2 + q_c^2 - \epsilon_c - \mu B - (q_o^2 - q_c^2 - \epsilon_c - \mu B) \sec 2\theta} / \sqrt{2} \tag{x}
\]

are the eigen wave number associated with the states \(|+\rangle\) and \(|-\rangle\), respectively.

Solving Eq. \([v]\) for a finite \(E_m\), the relative coordinate wave function of the Feshbach molecule is given by

\[
\begin{align*}
\text{For } r > r_0:\quad & |\psi_r\rangle = A_+ e^{\frac{\epsilon_c}{r}} |\psi_o\rangle, \tag{x} \\
\text{For } r < r_0:\quad & |\psi_r\rangle = A_+ \frac{\sin q_+ r}{r} |+\rangle + A_- \frac{\sin q_- r}{r} |-\rangle. \tag{xi}
\end{align*}
\]

where \(\gamma = (q_o^2 - \epsilon_m)^{1/2}\). The constants \(A_o, A_+\) and \(A_-\) are obtained by means of the boundary conditions \(\psi_o(r_0) = 0, (\psi_o(r^-_c) = \psi_o(r^+_c)\) and the normalization-to-unity \(\langle \psi_r | \psi_r \rangle = 1\). The energy eigenvalue equation

\[
-\epsilon_m = \frac{\hat{q}_+ \cos^2 \theta}{\tan q_+ r_0} + \frac{\hat{q}_- \sin^2 \theta}{\tan q_- r_0}, \tag{xii}
\]

is determined by the condition \(\psi_o(r_0)/\psi_c(r_0) = \psi_c(r_0)/\psi_o(r_0)\).

In the weak coupling regime between the open and closed channels, it is legitimate to assume that \(\Omega \ll q_o^2 q_c^2 - \epsilon_c - \mu B\) and \(q_o^2 q_c^2 + \epsilon_c + \mu B\), such that \(\theta \ll 1, q_+ \approx q_o, q_- \approx \sqrt{\epsilon_m - \epsilon_c - \mu B}\). In this limit, the closed channel contribution, which support the foreign bound state, is relevant only when it is close to the continuum and hence \(\epsilon_c + \mu B \ll q_o/r_0\). In that case, the last term in Eq. \([viii]\) diverge, which implies that \(\sin \sqrt{\epsilon_m - \epsilon_c - \mu B} \approx 0\). Therefore, by performing the first order expansion on the last term of Eq. \([viii]\) and assuming that the middle term is roughly a constant \((r_0 - a_{bg})^{-1}\), the approximated scattering length, Eq. \((3)\) in the main text, is obtained with

\[
\Delta B = \frac{\gamma \hbar^2}{\mu m} (a_{bg} - r_0) \tag{xiii}
\]

\[
B_{res} = -\mu^{-1} E_c + \Delta B, \tag{xiv}
\]

being the resonance width and the resonance position, respectively, \(a_{bg}\) is the scattering background and \(\gamma = 2q_o^2 \theta^2/\epsilon_o\). Since, in regime of bound states \(E_r < 0\) both channels are near the continuum, i.e. \(|a_{bg}| \gg 0\) and \(|\epsilon_c| \ll q_o/r_0\), performing the first order expansion on the last term of Eq. \([xiii]\) leads to the eigenenergy equation

\[
(\epsilon_m + \epsilon_c + \mu B) \left(\sqrt{\epsilon_m - \frac{1}{a_{bg} - r_0}}\right) = \gamma, \tag{xv}
\]

where \(E_m = \hbar^2 \epsilon_m/m\) is the binding energy.

Some parameters that characterize the model for the \(6^6\)Li\(_2\) (of mass \(m = 6.02\) u) have been experimentally determined in Ref. \([2]\):
where \(a_0\) is the Bohr radius, \(\mu_B\) the Bohr magneton and \(r_0\) is derived in [5]. The remaining parameters are inferred by the model using the weak coupling approximation:

\[
\begin{array}{cccc}
  r_0(a_0) & B^{\text{res}}(G) & \Delta B(G) & a_{bg}(a_0) & \mu(\mu_B) \\
  29.9 & 834.15 & 300 & -1405 & 2.0
\end{array}
\]

The parameter which characterizes the Feshbach strength \(\gamma\) was obtained using Eq. (xiii), the closed channel energy \(E_c\) using (xiv), and the even wave numbers \(q_c\) and \(q_o\) solving numerically the equations

\[
\frac{1}{r_0 - a_{bg}} = \sqrt{q_c - q_c \cos^2 \theta} \frac{\cos \theta}{\tan q_c r_0},
\]

with \(\theta = \sqrt{r_0 \gamma / 2q_c^2}\), and

\[
\frac{1}{r_0 - a_{bg}} = \sqrt{q_o \cos^2 \theta} \frac{\cos \theta}{\tan q_o r_0},
\]

respectively.

### Schmidt decomposition

Due to the cylindrical symmetry of the two-body system that we use, the ground state wave function \(\psi\) depends essentially on the radial coordinates of the atoms \(r_1\) and \(r_2\), and the inter-atomic angle \(\gamma\), such that \(R = \sqrt{r_1^2 + r_2^2 + 2r_1r_2 \cos \gamma / 2}\) and \(r = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \gamma}\). Thus, the wave function can be expanded in terms of the Legendre polynomial as

\[
\Psi(r_1, r_2, \cos \gamma) = \sum_{l} \alpha_l(r_1, r_2) P_l(\cos \gamma), \tag{xviii}
\]

where the functions \(\alpha_l(r_1, r_2)\) are given by

\[
\alpha_l(r_1, r_2) = \frac{2l + 1}{2} \int_0^\pi d\gamma \Psi(r_1, r_2, \cos \gamma) P_l(\cos \gamma) \sin \gamma. \tag{xix}
\]

Using the spherical harmonics addition theorem \((2l + 1) P_l(\cos \gamma) = 4\pi \sum_{m=-l}^{m=l} Y^*_{lm}(\theta, \varphi) Y_{lm}(\theta, \varphi)\), we have that

\[
\Psi(r_1, r_2) = 4\pi \sum_{l} \alpha_l(r_1, r_2) \frac{2l + 1}{2l + 1} Y^*_{lm}(\theta, \varphi) Y_{lm}(\theta, \varphi). \tag{xx}
\]

Note that this equation has the angular part already in the Schmidt form. To complete the Schmidt decomposition we have to perform the diagonalisation of the spatially discretized function \(f_l(r_1, r_2) = r_1r_2 \alpha_l(r_1, r_2)\) for each \(l\), that is

\[
f_l(r_1, r_2) = \sum_{n=0}^{n_{\text{max}}} k_{nl} u_{nl}(r_1) v_{nl}(r_2), \tag{xxi}
\]

where \(k_{nl}\) are the eigenvalue of \(f_l\), and \(u_{nl}\) and \(v_{nl}\) their corresponding eigenvectors. The prefactor \(r_1r_2\) is necessary to ensure the correct normalization. That is, we need to diagonalize the matrix \(M_{ij} = \Delta r f_j(\Delta r \cdot i, \Delta r \cdot j)\) with \(\Delta r = r_{\text{max}} / n_{\text{max}}\) and \(i, j = 1, 2, \ldots, n_{\text{max}}\). The position \(r_{\text{max}}\) should be chosen as large as possible in the range where the wave functions are mainly confined. By using the \(n_{\text{max}}\) eigenvalues, \(\kappa_{nl}\), and eigenvectors, \(u_{nl}(r_1)\) and \(v_{nl}(r_2)\), of \(M_{ij}\) together with Eq. (xxi), the Schmidt decomposition of the wave-function reads

\[
\Psi(r_1, r_2) = \sum_{n=0}^{n_{\text{max}}} \sum_{l=0}^{l_{\text{max}}} \sum_{m=-l}^{l} \sqrt{\lambda_{nl}} u_{nl}(r_1) v_{nl}(r_2), \tag{xxii}
\]

where the \(2l + 1\) degenerated Schmidt coefficients are given by \(\lambda_{nl} = 16\pi^2 \kappa_{nl}^2 / (2l + 1)^2\), and the single fermion eigenstates by \(\phi_{nlm}^{(1)}(r_1) = u_{nl}(r_1) Y_{lm}(\theta, \varphi)\) and \(\phi_{nlm}^{(2)}(r_2) = v_{nl}(r_2) Y_{lm}(\theta, \varphi)\), which form complete and orthonormal sets,

\[
\int dr_1^* \int dr_2^* \Psi(r_1, r_2) \Psi^*(r_1', r_2') \phi_{nlm}^{(1)}(r_1') = \lambda_{nl} \phi_{nlm}^{(1)}(r_1'),
\]

\[
\int dr_1^* \int dr_2^* \Psi(r_1, r_2) \Psi^*(r_1', r_2') \phi_{nlm}^{(2)}(r_2') = \lambda_{nl} \phi_{nlm}^{(2)}(r_2').
\]

Since the open and closed channel states, \(|a\) and \(|c\), are orthogonal, the Schmidt decomposition (xxii) applies separately to their respective wave functions \(\psi_R(R)\psi_o(r)\) and \(\psi_R(R)\psi_c(r)\). Therefore, the resulting Schmidt coefficient distribution which describes state \(|\psi\rangle\), is given by the join distribution \(\{\lambda_{nl}^o, \lambda_{nl}^c\}\). We also introduce a single global label \(j\) to characterize the state \(|\Psi\rangle\), which is derived in [5]. The remaining parameters are in-

FIG. 4: Normalization of the wave function \(|\Psi\rangle\) using the discretization method of Ref. 3 with \(n_{\text{max}} = 350\), \(l_{\text{max}} = 79\), \(r_{\text{max}} = 83338 \cdot a_0\) and \(\omega = 2\pi \cdot 10^9\) Hz, as a function of \(1 / k_p a = (16/9\pi)^{1/3} / a\) for \(N = 1\)

The numerical computation of the Schmidt distribution of \(|\Psi\rangle\) for plotting figures 2 and 3 in the main text.
and Fig. SM 4 was performed with $\omega = 2\pi \cdot 10^4$ Hz, $n_{\text{max}} = 350$, $l_{\text{max}} = 79$ and $r_{\text{max}} = 83338 \cdot a_0 \approx 6 \cdot \sigma$. Note that this characteristic length of the relative coordinate $r_{\text{max}}$ is larger than the harmonic oscillator length $2\sigma$. The normalization of the wave function for these parameters is larger than $\langle \Psi | \Psi \rangle \approx \sum_{S}^{S} \lambda_o^S > 0.986$ in the range $3 > 1/k_F a > 0.19$, see Fig. SM 4. Close to the unitary limit, the contribution of the closed channel increases with a consequently abrupt decay of the state normalization.

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