Bose-Einstein Condensate of Trimers Dressed by Atom-Dimer Cooper Pairs

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We theoretically examine the neutral atom-molecule analogue of the anomalous quantum correlations between degenerate electrons, i.e., Cooper pairs, that are responsible for superconductivity. Based on rogue dissociation of triatomic molecules (trimers) into opposite-momentum pairs of atoms and diatomic molecules (dimers) via a photoassociation or Feshbach resonance, we find a superfluid transition to a Bose-Einstein condensate of trimers dressed by atom-dimer Cooper pairs, at a critical temperature in reach of present ultracold technology.

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Exotic ultracold molecules are all the rage. For example, there are prospects for quadratomic molecules via photoassociation of ultracold polar molecules, and evidence of forbidden molecular transitions in ultracold Rydberg atoms. Going colder to Bose-Einstein condensates (BECs), there are opportunities for amplified selectivity in photodissociation of triatomic molecules, and mesoscopic molecular ions in BEC doped with an charged impurity. Lately this frenzy has surrounded ultracold and condensate diatomic molecules emerging from a Fermi sea of atoms.

In basic magnetoassociation, a molecule is created when one atom from a colliding pair undergoes a spin flip in the presence of a magnetic field tuned near a Feshbach resonance. A similar molecular state arises when two atoms absorb a photon tuned near a photoassociation resonance. The statistics of neutral molecules are determined by the number of neutrons in the nuclei of the constituent atoms: odd for fermions, even for bosons. Resonant association thus presents an unusual opportunity to change the particle statistics, leading to cooperative fermion behavior. For example, a photoassociation or Feshbach resonance could deliver the neutral-atom analogue of the anomalous quantum correlations between electrons (Cooper pairs) responsible for superconductivity. Magnetoassociation experiments are presently poised to realize this regime.

Meanwhile, attention is turning to resonant association in Bose-Fermi mixtures of atoms, and the subsequent atom-molecule Cooper pairing. However, the most optimistic superfluid transition temperature is an order of magnitude below what is currently feasible. Based on rogue dissociation of triatomic molecules (trimers) into opposite-momentum pairs of atoms and diatomic molecules (dimers), we therefore report a high-temperature superfluid transition to a Bose-Einstein condensate of trimers dressed by atom-dimer Cooper pairs. Upon diagonalizing the Hamiltonian, we present theory on the trimer-molecule binding energy and the superfluid transition temperature. For Li dimers, the superfluid transition should occur at about a tenth the atomic Fermi temperature.

In its simplest guise, the theory of collective resonant association is a two-mode model, analogous to second-harmonic-generated photons, which couples zero-momentum atomic and molecular condensates. Rogue transitions to the continuum of noncondensate atomic modes occur because dissociation of a zero-momentum condensate molecule need not result in zero-momentum condensate atoms, but may just as well deliver two noncondensate atoms with equal and opposite momentum. Rogue dissociation ultimately leads to anomalous quantum correlations between atoms, which are the analogue of Cooper pairs. An immediate consequence of said correlations is Ramsey fringes between atoms and molecules. The same intuition will also prove useful here.

We model an ideal degenerate mixture of fermionic atoms and dimer molecules coupled by either a Feshbach or photoassociation resonance to bound trimer molecules. An ideal gas is chosen mainly because off-resonant particle-particle interactions are generally too weak for practical purposes. The initial fermionic atom-dimer state could be prepared using a Raman scheme for photoassociating a degenerate Bose-Fermi mixture of atoms, and selectively removing the leftover bosons. The atom-dimer ↔ trimer resonance is expectedly well resolved so that, once the initial atom-dimer state has been created, transitions involving three free atoms are avoided. In contrast to the all-boson case, ultracold transitions that involve a free bosonic atom are Pauli blocked, i.e., the two identical fermionic constituents of a given trimer may not form a bound state.

In second-quantization parlory, a particle of mass and momentum ℏk is described by the creation operator . The Greek index corresponds mnemonically to the number of constituent atoms a given particle contains: 3 for bosonic trimers, 2 for fermionic dimers, and 1 for fermionic atoms. All operators obey their (anti)commutation relations. The microscopic Hamiltonian...
The condensate mean-field is
\[
\frac{H}{\hbar} = \sum_{k, \sigma} \left[ (\varepsilon_{k, \sigma} - \mu_0) a_{k, \sigma}^{\dagger} a_{k, \sigma} + \frac{K}{\sqrt{v}} \sum_{k, k'} \left( a_{k+k', 3}^{\dagger} a_{k, 2}^{\dagger} a_{k', 1} a_{k, 2} + \text{H.c.} \right) \right].
\] (1)

The free-particle energy is defined by \( \hbar \varepsilon_{k, \sigma} = \hbar^2 k^2 / 2m_\sigma \), and the chemical potential by \( \hbar \mu_0 \). In particular, the molecular chemical potential is defined by \( \mu_3 = 2\mu - \delta_0 \), where the bare detuning \( \delta_0 \) is a measure of the binding energy of the trimer with \( \delta_0 > 0 \) taken as above threshold. The (mode-independent) atom-molecule coupling is \( K \), and \( V \) is the quantization volume.

The key realization is how to cast the Hamiltonian into a readily diagonalized form. Consider a time-dependent unitary transformation, which leaves the physics unchanged providing \( H \rightarrow U^\dagger H U - iU^\dagger \partial_t U \). Given the generator \( U = \Pi_{k, \sigma} \exp[-i\varepsilon_{k, \sigma} a_{k, \sigma}^{\dagger} a_{k, \sigma}] \), then \( u_{k,3} = u_{k,1} + u_{k,2} \) implies \([H, U] = 0\) and, thus, \( H \rightarrow H - iU^\dagger \partial_t U \). Appropriately armed, the unitary transformation specified by \( u_{k,1(2)} = [\varepsilon_{k,1(2)} - \varepsilon_{k,2(1)}]/2 \), which conveniently corresponds to the special case \( u_{k,3} = 0 \), leaving the trimer term unchanged. The new Hamiltonian reads:
\[
\frac{H}{\hbar} = \sum_{k} \left[ (\varepsilon_{k, \sigma} + \delta_0 - 2\mu) a_{k, 3}^{\dagger} a_{k, 3} + (\varepsilon_{k} - \mu) a_{k, \sigma}^{\dagger} a_{k, \sigma} \right] - \frac{K}{\sqrt{v}} \sum_{k, k'} \left( a_{k+k', 3}^{\dagger} a_{k, 2}^{\dagger} a_{k', 1} a_{k, 2} + \text{H.c.} \right),
\] (2)

where the reduced free-particle energy is \( \hbar \varepsilon_{k} = \hbar^2 k^2 / 4m^*, \) with \( 1/m^* = 1/m_1 + 1/m_2 \). Also, chemical equilibrium has been incorporated as \( 2\mu = \mu_1 + \mu_2 \).

We may now make a transformation to a dressed basis:
\[
\begin{pmatrix}
\alpha_{k, 1} \\
\alpha_{k, 2}
\end{pmatrix}
= \begin{pmatrix}
\cos \theta_k & e^{-i\varphi_k} \sin \theta_k \\
-e^{i\varphi_k} \sin \theta_k & \cos \theta_k
\end{pmatrix}
\begin{pmatrix}
\alpha_{k, 1} \\
\alpha_{k, 2}
\end{pmatrix},
\] (3a)

\[\alpha_{k, 3} = a_{k, 3} + \sqrt{\Phi} \delta_{k, 0},\] (3b)

where \( \delta_{k, 0} \) is the Kronecker delta-function,
\[
\frac{H}{\hbar} = (\delta_0 - 2\mu) V |\Phi|^2 + \sum_{k} \left[ (\varepsilon_{k, \sigma} + \delta_0 - 2\mu) a_{k, 3}^{\dagger} a_{k, 3} + \omega_k \left( a_{k, 1}^{\dagger} a_{k, 1} + a_{k, 2}^{\dagger} a_{k, 2} - 1 \right) \right].
\] (4)

The condensate mean-field is \( \langle a_{0,3} \rangle / \sqrt{V} = e^{i\varphi} |\Phi| \), the mixing angle is tan \( 2\theta_k = |\Phi| K / (\varepsilon_k - \mu) \), the quasiparticle frequency is \( \omega_k^2 = (\varepsilon_k - \mu)^2 + |\Delta|^2 \), and the gap is \( |\Delta| = K |\Phi| \). The Hamiltonian is now lowest-order diagonal.

Since the contribution of rogue dissociation to resonant association can be written as the set of all one-loop Feynman diagrams, and since applying the canonical transformation is in fact equivalent to summing over that set, then our generic intuition is clearly applicable. Broadly put, the lowest-energy configuration of the system is a molecular Bose-Einstein condensate dressed by anomalously correlated pairs of equal and opposite momentum. More precisely, sweeping the detuning continuously evolves this superposition from all trimers well below threshold, to an admixture of trimers and atom-dimer Cooper pairs near threshold, to all atom-dimer Cooper pairs well above threshold.

To illustrate, consider the mean-field Heisenberg equations for the bosonic operator \( a_{0,3} \) and the anomalous pair-correlation operator \( C_k = a_{k, 1} a_{-k, 2} \) (sans chemical potential and collective enhancement):
\[
\frac{i}{\hbar} \frac{d}{dt} \langle a_{0,3} \rangle = \delta_0 \langle a_{0,3} \rangle - \frac{K}{\sqrt{v}} \sum_k \langle C_k \rangle, \tag{5a}
\]
\[
\frac{i}{\hbar} \frac{d}{dt} \langle C_k \rangle = 2\varepsilon_k \langle C_k \rangle - \frac{K}{\sqrt{v}} \langle a_{0,3} \rangle. \tag{5b}
\]

Below threshold, simple Fourier analysis delivers the binding energy, \( \hbar \omega_B < 0 \), of the Bose-condensed trimers:
\[
\omega_B - \delta_0 - \Sigma(\omega_B) + i\eta = 0, \tag{6}
\]

where \( \Sigma(\omega_B) \) is the self-energy of the Bose molecules and \( \eta = 0^+ \). Incidentally, we show elsewhere that the real poles of equation (6) fit the Regal et al. data for the binding energy of \( 40K \) molecules, and similar measurements for a system of trimers would uniquely determine the parameters of the present theory. On the other side of threshold, the critical temperature for the transition to effectively all superfluid atom-dimer pairs is derived from Eq. (5a):
\[
T_c/T_F \approx \exp \left(-\frac{\pi/4}{k_F |a_R|} \right). \tag{7}
\]

Here the resonant atom-dimer scattering length is \( a_R = -(4\pi m^*/\hbar)K^2 / \delta_0 \). Also, we have taken a single Fermi wavevector, \( K_F \), for the atoms and the dimers, i.e., \( \mu_1 + \mu_2 = \mu_{1(2)} m_{3(2)} / m^* \); assuming that the particles see the same trap, adjusted for mass differences, equal Fermi wavevectors are realized if the number of atoms and dimers satisfy \( N_2/N_1 = (m_1/m_2)^{3/2} \). The effective Fermi temperature is \( k_B T_F / \hbar = (\mu_1 + \mu_2) m^* / \sqrt{m_1 m_2} \), or \( T_F = T_F^{(3)} / \sqrt{m_1 m_2} \). Last but not least, it is easy to show \( \Delta \propto T_c \), so that \( |\Phi| \propto \exp(-\pi/4k_F |a_R|) \), and the trimer part of the dressed BEC-pair admixture becomes larger near threshold (increasing \( |a_R| \)), as expected.

Whereas the below-threshold regime of a trimer condensate is no doubt of interest (\( a_R > 0 \)), both as a precursor to fermionic superfluidity and in its own right, we
keep our focus on attractive systems. The strongly interacting regime is defined by \( k_F |a_G| \sim 1 \), indicating a transition to predominantly atom-dimer Cooper pairs at the critical temperature \( T_c \sim 0.45 T_F \). Using \( m_3 = m_1 + 2m_1 \) as an example, which is akin to a system of \( ^6\)Li atoms and \( ^7\)Li-\( ^6\)Li dimers, the required dimer-atom fraction is \( N_2 / N_1 = 0.31 \), the ratio of the effective and atomic Fermi temperatures \( T_F = 0.7T_F^{(1)} \), and the critical temperature \( T_c \sim 0.3T_F^{(1)} \). Although Eq. (4) is of dubious validity for \( T_c \lesssim T_F \), it confirms that resonant association should in principle drive superfluid pairing between atoms and dimer molecules at transition temperatures within reach of present ultracold technology.

To rigorously identify the critical temperature for the superfluid transition, it is necessary to go beyond the effective atom-dimer theory, and explicitly include the bosonic molecular state. Continuing to focus on a system of \( ^6\)Li atoms and \( ^7\)Li-\( ^6\)Li dimers, we return to the Hamiltonian (4) and set \( \epsilon_{k,3} \sim \frac{1}{2} \epsilon_k \). We also introduce a second molecular state, which can arise because large detuning from one state brings the system into the neighborhood of another bound state, or because of the presence of a scattering resonance. The Hamiltonian (4) is adapted simply by making the substitution \( \delta_0 \rightarrow \delta_{0,1} (\Phi \rightarrow \Phi_1, \mathcal{K} \rightarrow \mathcal{K}_1) \), and summing over the index \( l \); also, the gap becomes \( |\Delta| = \mathcal{K}_1 |\Phi_1| + \mathcal{K}_2 |\Phi_2| \). Here \( \mathcal{K}_2 \gtrsim \mathcal{K}_1 \), and the system is tuned between the two levels so that \( \delta_2 > 0 \) and \( \delta_1 < 0 \). The thermodynamic pressure is the centerpiece of this calculation, and is obtained from the partition function \( \Xi = \text{Tr} \exp (-\beta H) \):

\[
p = -\sum_l (\delta_{0,l} - 2\mu) |\Phi_l|^2 + V^{-1} \sum_k (\omega_k + \mu - \epsilon_k) \\
+ 2(\beta V)^{-1} \sum_k \ln (1 + e^{-\beta \omega_k}) \\
- (\beta V)^{-1} \sum_{k,l} \ln \left\{ 1 - \exp \left[ \beta (2\mu - \delta_{0,l} - \frac{1}{2} \epsilon_k) \right] \right\},
\]

where \( 1/\beta = k_B T / \hbar \). The chemical potential is determined from the condition \( \partial p/\partial |\Phi_l| |_{\mu,T} = 0 \):

\[
(\delta_l - 2\mu) |\Phi_l| = 2\Sigma_l |\Delta| + \frac{\mathcal{K}_l |\Delta|}{2V} \sum_k \frac{1}{\omega_k} \tanh \frac{1}{2} \beta \omega_k. \tag{9a}
\]

Renormalization is via the resonant self-energy \( \Sigma_l (0) \), meaning the summation is ultraviolet convergent and the physical detuning \( \delta_l \) replaces the bare detuning. Given the chemical potential, the density of the system \( \rho \equiv \langle N \rangle / V \) determines the gap according to \( \rho = \partial p/\partial |\Phi_l| |_{\mu,T} \Phi \):

\[
\rho = 2 \sum_l |\Phi_l|^2 + \frac{2}{V} \sum_{k,l} \exp \left[ \beta \left( \frac{1}{2} \epsilon_k + \delta_l - 2\mu \right) \right] \frac{1}{\omega_k} \\
+ \frac{1}{V} \sum_k \frac{\omega_k + \mu - \epsilon_k + (\omega_0 - \mu + \epsilon_k) e^{-\beta \omega_k}}{\omega_k [1 + e^{-\beta \omega_k}]}. \tag{9b}
\]

![FIG. 1: Onset of the superfluid transition to a Bose-Einstein condensate of trimers formed by anomalous atom-dimer pairs. The non-zero superfluid gap clearly lowers the system energy compared to the normal state (dashed curve). When the detuning is large and positive (\( \delta_2 \gg \sqrt{\mathcal{K}_2} \)), such as here, the system is mostly rogue pairs with a negligible fraction of trimers.](http://example.com/figure1)

The algebraic system (9) is sufficient to numerically determine the chemical potential as a function of temperature, which should display a characteristic cusp at the onset of superfluidity. Physically, a cusp arises because the superfluid BEC-pair dressed state is lower in energy than the normal state, implying the concurrent appearance of a non-zero gap. This intuition is confirmed in Fig. 1. For positive detunings large compared to the collective-enhanced coupling (\( \delta_2 \gg \sqrt{\mathcal{K}_2} \) with \( \delta_1 \approx -\delta_2 \)), the effective atom-dimer theory (7) with \( k_F |a_G| = 1/2 \) is an excellent working approximation. Also, the fraction of trimer is puny (\( \sim 10^{-7} \)), as per the large detuning. Any s-wave collisional interactions are negligible compared to the detuning, justifying the ideal-gas assumption. The trap, albeit omitted, should actually favor the occurrence of superfluid pairing (15).

Dimer molecules created near a Feshbach resonance are highly vibrationally excited and, thus, characteristically long-range (Köhler et al. [17]). Fermion-composite dimers are consequently long-lived due to Pauli-suppressed vibrational relaxation [15], and there is no reason to expect otherwise from Feshbach trimer states. In photoassociation, a two-color Raman scheme is required to avoid spontaneous decay: a laser couples the atoms to an electronically-excited intermediate trimer state, a second laser couples the system to a ground-electronic trimer manifold, and the intermediate trimer state is well-detuned. Long-range states are available with photoassociation, although a Raman scheme also allows access to stable lower-lying vibrational levels, which are much smaller and less understood. Nevertheless, the
molecular fraction is negligibly small when the system is well above the appropriate threshold, diminishing the chance for spontaneous decay for any kind.

For a signature, note that Cooper pairing was suggested to explain how nuclei with even numbers of nucleons can have a larger excitation energy than nuclei with odd numbers of nucleons. The presence of anomalous atom-dimer correlations should similarly blueshift the resonant frequency of a dimer-dissociating photon by an amount proportional to the gap, in contrast to the otherwise red-shifted photodissociation photon (see also boson blueshift). Physically, the increased frequency comes about because, in order to dissociate a dimer molecule, an extra amount of energy, specifically, the gap energy, is needed to break any anomalous correlations. If the dissociating light is weak enough to justify lowest-order free-bound transitions, the blueshift should dominate the redshift.

In conclusion, we reinforce the idea that statistics need not be an issue in resonant association: each of the systems (Bose, Fermi, Bose-Fermi) is described by the same basic Heisenberg equations of motion, and will respond as a unit to form molecules in mostly-complete cooperation. Moreover, while it is not entirely clear how many constituents the association bound states may in practice contain, the limit is certainly not two. Granted, at this stage it is difficult to predict timescales, but in this respect the quantum optics approach–based on ratios of parameters not parameters–has a decided advantage. This line of thought is well above the appropriate threshold, diminishing the chance for spontaneous decay for any kind.

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