Formation of Pairing Fields in Resonantly Coupled Atomic and Molecular Bose-Einstein Condensates

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We show that pair correlations may play an important role in the dynamical properties of a Bose-Einstein condensed gas composed of an atomic field resonantly coupled with a condensed field of molecular dimers. Specifically, pair correlations in this system can dramatically modify the coherent and incoherent transfers between the atomic and molecular fields.

Superfluidity and long-range order are usually identified with a complex-valued order parameter defined as the expectation value of the field operator. In the case of a dilute Bose gas, the evolution of the order parameter is given in the mean-field approximation by the well-known Gross-Pitaevskii equation. Recently, this equation has been extensively applied to studies of the zero-temperature collective behavior of metal-alkali Bose-Einstein condensates confined in magnetic traps. Quantitative agreement has been found between theory and experiment for a wide range of distinct phenomena [1,2].

Although identical in form to a nonlinear Schrödinger equation, it is notable that the Gross-Pitaevskii equation does not by itself describe the full evolution of the quantum state. In general, a complete kinetic description requires knowledge of the evolution of a hierarchy of correlation functions, and not just the evolution of the expectation value of the field [3]. In particular, in low temperature systems, it is well known that pairing fields associated with two-particle correlations can play an important role. In a quantum degenerate Fermi gas, pairing may radically alter the equilibrium properties, giving rise to superfluidity in ^{3}He and superconductivity in electron systems. Correlations can also be important in Bose systems. For example, squeezed states of light — formed when photons are generated in pairs in nonlinear media — have been studied extensively in the field of quantum optics [4].

In this Letter, we elucidate the important role of pair correlations on the macroscopic dynamics of a dilute Bose-Einstein condensate composed of resonantly coupled atoms and molecules. This extension leads to significant deviations from a simple mean-field picture [5–8]. We find that proper treatment of correlations rapidly damps the giant atom-molecule oscillations predicted by mean-field theory. The inevitable consequence of the damping is an increase in the density of the thermal cloud. This behavior also resolves the conceptual difficulty associated with the rapid atom-molecule oscillations — how can pairs of atoms find each other rapidly enough to form molecules at the predicted rate?

The atom-molecule coupling may be generated experimentally [9,10] by tuning the strength of an external magnetic field in the proximity of a Feshbach resonance (see Fig. 1). Two parameters characterize the Feshbach resonance: (i) the energy mismatch ϵ between the bound state and the zero energy edge of the continuum states for the colliding atom pair, and (ii) the inverse lifetime κ of the bound state. As an alternative, photoassociation may be used to directly generate the resonant coupling [11,12]. In photoassociation, a two-photon Raman transition is used to couple the atomic continuum states to a specific bound molecular level. In that case ϵ represents the detuning energy of the Raman lasers from the atom-molecule transition, and κ denotes the two-photon Rabi frequency proportional to the laser intensities and to the usual overlap integrals.

A Hamiltonian for this coupled atom-molecule system may be written as

$$\hat{H} = \int d^3\boldsymbol{x}\, \hat{\psi}_a^\dagger(\boldsymbol{x}) H_a(\boldsymbol{x}) \hat{\psi}_a(\boldsymbol{x}) + \hat{\psi}_m^\dagger(\boldsymbol{x}) H_m(\boldsymbol{x}) \hat{\psi}_m(\boldsymbol{x})$$

$$+ \frac{U_{aa}}{2} \int d^3\boldsymbol{x}\, \hat{\psi}_a^\dagger(\boldsymbol{x}) \hat{\psi}_a^\dagger(\boldsymbol{x}) \hat{\psi}_a(\boldsymbol{x}) \hat{\psi}_a(\boldsymbol{x}) + U_{am} \int d^3\boldsymbol{x}\, \hat{\psi}_a^\dagger(\boldsymbol{x}) \hat{\psi}_m^\dagger(\boldsymbol{x}) \hat{\psi}_m(\boldsymbol{x}) \hat{\psi}_a(\boldsymbol{x})$$

$$+ \frac{U_{mm}}{2} \int d^3\boldsymbol{x}\, \hat{\psi}_m^\dagger(\boldsymbol{x}) \hat{\psi}_m^\dagger(\boldsymbol{x}) \hat{\psi}_m(\boldsymbol{x}) \hat{\psi}_m(\boldsymbol{x}) + \frac{g}{2} \int d^3\boldsymbol{x}\, \hat{\psi}_m^\dagger(\boldsymbol{x}) \hat{\psi}_a(\boldsymbol{x}) \hat{\psi}_a(\boldsymbol{x}) + \text{H.c.}, \tag{1}$$

where $\hat{\psi}_a(\boldsymbol{x})$ and $\hat{\psi}_m(\boldsymbol{x})$ are bosonic field operators which annihilate atoms or molecules, respectively. The mean-field potential arising from binary atomic collisions is determined by $U_{aa} = 4\pi\hbar^2 a/m$, where m is the atomic

mass, and a is the scattering length for atom-atom collisions. Equivalent definitions apply for U_{am} and U_{mm}, corresponding to atom-molecule collisions and molecule-molecule collisions. The interconversion of atom pairs into
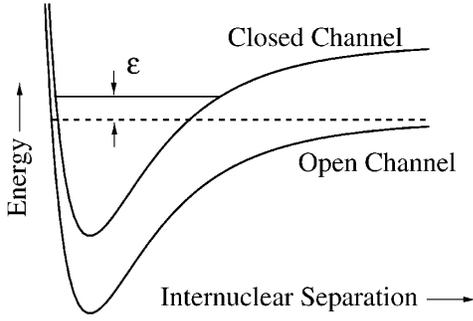
FIG. 1. Feshbach resonance. Atoms collide with relative kinetic energy near zero as indicated by the dashed line. This energy is quasidegenerate with a bound state in a closed channel potential. Typically, ϵ can be tuned experimentally by changing the magnitude of an external magnetic field.

molecules is characterized by $g = \sqrt{\kappa U_{aa}}$ [5]. The free Hamiltonians are $H_a(x) = -\hbar^2 \nabla^2/2m + V_a(x) - \mu_a$ and $H_m(x) = -\hbar^2 \nabla^2/4m + V_m(x) - \mu_m$, where we include $V_a(x)$ and $V_m(x)$ for generality to allow for the possibility of external potentials. Here the chemical potentials of the atomic and molecular fields are denoted by μ_a and μ_m, respectively, such that $\epsilon = \mu_m - 2\mu_a$.

We derive a mean-field description according to the following prescription. For the molecules, we replace the field operator by its mean value, $\phi_m(x) = \langle \hat{\psi}_m(x) \rangle$, thereby assuming a classical condensed field. Anticipating that pairing of atoms will play an intrinsic dynamical role, we treat the atomic field in a more detailed manner, incorporating both the mean value of the field, $\phi_a(x) = \langle \hat{\psi}_a(x) \rangle$, and the single-time Green's functions for normal fluctuations, $G_N(x, y) = \langle \hat{\chi}_a^\dagger(y) \hat{\chi}_a(x) \rangle$, and anomalous fluctuations, $G_A(x, y) = \langle \hat{\chi}_a(y) \hat{\chi}_a(x) \rangle$, where $\hat{\chi}_a(x) = \hat{\psi}_a(x) - \phi_a(x)$. Deriving the first-order Hartree-Fock-Bogoliubov theory then gives the following equations of motion for the condensates:

$$i\hbar \frac{d\phi_a(x)}{dt} = [H_a(x) + \Upsilon_a(x)]\phi_a(x) + \Theta(x)\phi_a^*(x),$$

$$i\hbar \frac{d\phi_m(x)}{dt} = [H_m(x) + \Upsilon_m(x)]\phi_m(x) + \Phi(x), \quad (2)$$

with corresponding mean-field potentials

$$\Upsilon_a(x) = U_{aa}(|\phi_a(x)|^2 + 2G_N(x, x)) + U_{am}|\phi_m(x)|^2,$$

$$\Upsilon_m(x) = U_{am}(|\phi_a(x)|^2 + G_N(x, x)) + U_{mm}|\phi_m(x)|^2,$$

$$(3)$$

and coupling elements

$$\Theta(x) = U_{aa}G_A(x, x) + g\phi_m(x),$$

$$\Phi(x) = \frac{g}{2}(\phi_a(x)^2 + G_A(x, x)). \quad (4)$$

A concise representation for the evolution of the atomic fluctuations is given by

$$i\hbar \frac{d\mathcal{G}}{dt} = \Sigma\mathcal{G} - \mathcal{G}\Sigma^\dagger, \quad (5)$$

with single-particle density matrix

$$\mathcal{G}(x, y) = \begin{pmatrix} \langle \hat{\chi}_a^\dagger(y)\hat{\chi}_a(x) \rangle & \langle \hat{\chi}_a(y)\hat{\chi}_a(x) \rangle \\ \langle \hat{\chi}_a^\dagger(y)\hat{\chi}_a^\dagger(x) \rangle & \langle \hat{\chi}_a(y)\hat{\chi}_a^\dagger(x) \rangle \end{pmatrix}, \quad (6)$$

and Bogoliubov self-energy of symplectic structure

$$\Sigma(x, y) = \begin{pmatrix} \tilde{H}(x, y) & \tilde{\Theta}(x, y) \\ -\tilde{\Theta}(x, y)^* & -\tilde{H}(x, y)^* \end{pmatrix}. \quad (7)$$

The 2×2 elements of $\Sigma(x, y)$ are each diagonal in x and y due to the implicit contact potential in Eq. (1). Accordingly, by defining $\tilde{H}(x, x) = H_a(x) + \tilde{\Upsilon}(x, x)$, the set of equations are closed by specifying

$$\tilde{\Upsilon}(x, x) = 2U_{aa}(|\phi_a(x)|^2 + G_N(x, x)) + U_{am}|\phi_m(x)|^2,$$

$$\tilde{\Theta}(x, x) = U_{aa}(|\phi_a(x)|^2 + G_A(x, x)) + g\phi_m(x). \quad (8)$$

As an example of the implementation of these equations, we apply the theory to consider a spatially uniform gas by the assumption that we may set to zero the external potentials, $V_a(x)$ and $V_m(x)$. In order to simplify the model as much as possible, we also discard the effects of background mean fields by setting to zero U_{aa}, U_{am}, and U_{mm}. Inclusion of these terms can be done in a straightforward manner (although renormalization of the low energy effective field theory is then slightly more involved) and does not change the essential predictions which follow. Because of translational symmetry, the resulting atomic and molecular condensates are spatially homogeneous, and the normal and anomalous densities, $G_N(x, y)$ and $G_A(x, y)$, depend only on the magnitude of the relative coordinate, i.e., $|x - y|$.

We convert the equations to dimensionless forms in the following manner. We define the number density n as the number of atoms plus twice the number of molecules per unit volume. Then $g\sqrt{n}$ denotes a characteristic coupling energy of the atomic and molecular mean fields. A dimensionless time τ can therefore be defined by $\tau = g\sqrt{n}\,t/\hbar$. A dimensionless coordinate $r = |x - y|/\zeta$ is associated with the length scale ζ corresponding to the formation of molecules from atom pairs. This is effectively a "molecular healing length" found by balancing the relative kinetic energy with the resonance coupling energy, i.e., $\hbar^2/2\mu\zeta^2 = g\sqrt{n}$, where $\mu = m/2$ is the reduced mass. By making systematic substitutions, $\phi_a = \phi_a(x)/\sqrt{n}$, $\phi_m = \phi_m(x)/\sqrt{n}$, $G_N(r) = G_N(x, y)/n$, $G_A(r) = G_A(x, y)/n$, and $\Delta = \epsilon/g\sqrt{n}$ gives the complete system of equations in dimensionless form

$$i \frac{d\phi_a}{d\tau} = \phi_a^* \phi_m ,$$

$$i \frac{d\phi_m}{d\tau} = -\phi_m \Delta + \frac{1}{2}(\phi_a^2 + G_A(r)|_{r=0}) ,$$

$$i \frac{dG_N(r)}{d\tau} = \phi_m G_A^*(r) - \phi_m^* G_A(r) ,$$

$$(9)$$

$$i \frac{dG_A(r)}{d\tau} = -\nabla_r^2 G_A(r) + \phi_m[2G_N(r) + \eta^{-1}\delta^{(3)}(r)] ,$$

where $\delta^{(3)}(r)$ is the isotropic three-dimensional Dirac delta function and we have defined $\eta = n\zeta^3$ as a diluteness parameter of the coupled atomic and molecular gas. There are explicitly conserved quantities in these equations corresponding to normalization (density of atoms plus twice the density of molecules), i.e.,

$$|\phi_a|^2 + G_N(r)|_{r=0} + 2|\phi_m|^2 = 1 , \qquad (10)$$

and energy density u (energy due to detuning and coupling plus the kinetic energy of the normal gas)

$$u = -\Delta|\phi_m|^2 + \mathrm{Re}[\phi_m^*(\phi_a^2 + G_A(r)|_{r=0})] \\ - \tfrac{1}{2}\nabla_r^2 G_N(r)|_{r=0} . \qquad (11)$$

Interestingly, Eq. (9) cannot be directly integrated as written. The delta function describes the *spontaneous* breakup of molecules into atom pairs. This process is reminiscent of the decay of an excited atom leading to the spontaneous emission of a photon. In that case, the interaction with the unoccupied vacuum modes of the radiation field gives both an energy width and an energy shift (Lamb shift) to the decaying state. Analogously in the atom-molecule system, there is an energy shift of the molecular state containing contributions from all diagrams representing the breakup of molecules into *virtual* atom pairs. The virtual atom pairs may form an intermediate state off the energy shell. Summing over the full spectrum of wave numbers for the pair gives an infinite shift to the molecular level.

This divergence is reconciled by noting that we have been inconsistent in not including the self-energy of the molecular quantum state in the original definition of the chemical potential μ_m. We carry out the renormalization in the following manner. We place an artificial bound on the momenta of the atom pair by replacing the delta function by a three-dimensional Gaussian of standard width σ_r normalized to have unit volume

$$\delta^{(3)}(r) \rightarrow (2\pi\sigma_r^2)^{-3/2} e^{-r^2/2\sigma_r^2}. \qquad (12)$$

Physically, this accounts for the fact that the real potential is not exactly a contact potential. The resulting energy shift is then finite and we derive its value according to the following prescription. We define a three-dimensional Fourier transform

$$G_A(k) = \int d^3r \, G_A(r) e^{-ir \cdot k}, \qquad (13)$$

which for the isotropic case is simplified to $G_A(k) = 4\pi k^{-1} \int_0^\infty r G_A(r) \sin(kr) \, dr$. As $k \to \infty$, an approximate equation for $G_A(k)$ using Eq. (9) is

$$i \frac{dG_A(k)}{d\tau} = k^2 G_A(k) + \frac{\phi_m}{\eta(k)} , \qquad (14)$$

where $\eta(k) = \eta \exp(\sigma_r^2 k^2/2)$. Arbitrarily taking $G_A(k) = 0$ at $\tau = 0$, the solution of this equation is

$$G_A(k) = \frac{-i}{\eta(k)} \int_0^\tau \phi_m(\tau') e^{ik^2(\tau'-\tau)} \, d\tau' \approx \frac{-\phi_m(\tau)}{k^2 \eta(k)} . \qquad (15)$$

Calculating the energy shift of the molecular level requires substituting this result into the evolution equation for $d\phi_m/d\tau$ in Eq. (9). Using the Fourier integral $G_A(r)|_{r=0} = (2\pi^2)^{-1} \int_0^\infty k^2 G_A(k) \, dk$, the resulting shift may be incorporated into a renormalized detuning Δ:

$$\Delta \rightarrow \Delta - \frac{\sqrt{2\pi}}{8\pi^2 \eta \sigma_r} . \qquad (16)$$

The end result of this analysis is that Eq. (9) is satisfactorily renormalized by making the two substitutions, Eqs. (12) and (16). The evolution of any observable will then be independent of the choice of σ_r, providing σ_r is chosen to be sufficiently small.

Although we have removed the ultraviolet divergence of the molecular state, we emphasize that there remains a width to the state in general which may be evaluated in the same second-order level of perturbation theory. Physically the width arises from a process by which an unbound molecule can spontaneously disintegrate into an atom pair with a possible continuum of energies. Atoms generated by such a spontaneous process acquire a random phase undetermined by the phase of the broken symmetry field. Therefore, while the Hamiltonian theory is reversible, the evolution of observables such as populations and quantum mechanical coherences may acquire the appearance of damping.
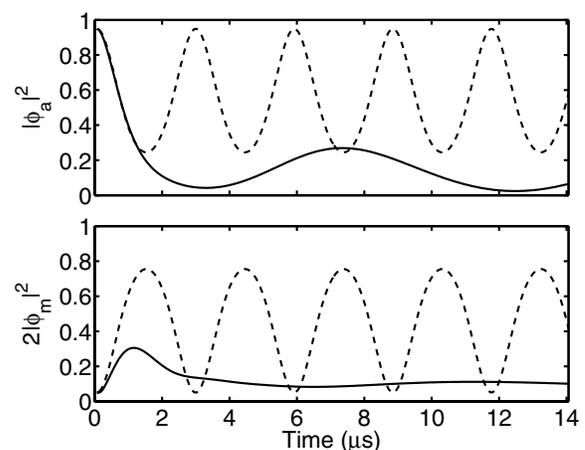
FIG. 2. Time evolution of the atomic condensate $|\phi_a|^2$ and molecular condensate $2|\phi_m|^2$ for solely mean-field theory (dashed lines) and for the Hartree-Fock-Bogoliubov theory (solid lines).
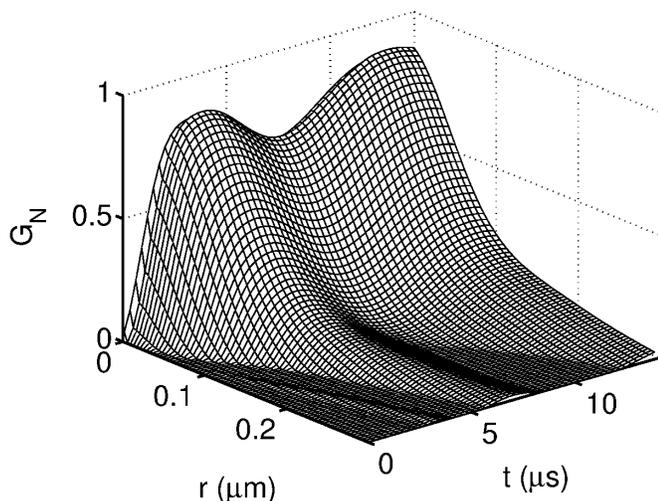
FIG. 3. Evolution of the normal density.

As a numerical example, we examine the ^{23}Na Feshbach resonance at 907 G [9]. For this system $\kappa = 2\pi\hbar \times 4.6$ MHz, and we consider the bound state to be on-resonance with the colliding atom pairs (i.e., $\Delta = 0$). Other parameters are the scattering length $a = 60a_0$, where a_0 is the Bohr radius, and we take a density of 10^{15} cm^{-3}. This gives a diluteness parameter of $\eta = 6 \times 10^{-2}$. In the simulation in Fig. 2 we show the evolution of the atomic and molecular condensate fields, comparing the Hartree-Fock-Bogoliubov theory we have derived with the predictions of mean-field theory. The initial condition is taken as 95% of the population in the atomic condensate and 5% in the molecular condensate.

The persistent large scale oscillations of the population of the atomic and molecular condensates as seen in a solely mean-field theory dampen out when the coupling to the normal gas is included. This is partly due to the fact that, when molecules are formed from atom pairs, the pair correlation function at that point is depleted, and is partly due to the possibility of spontaneous breakup of the gener-

ated molecules into the normal component of the gas. The damping of the population oscillations in this theory is intrinsic and not due to interactions with external reservoirs; e.g., relaxation of the molecules in highly excited vibrational states, or spontaneous emission in photoassociation.
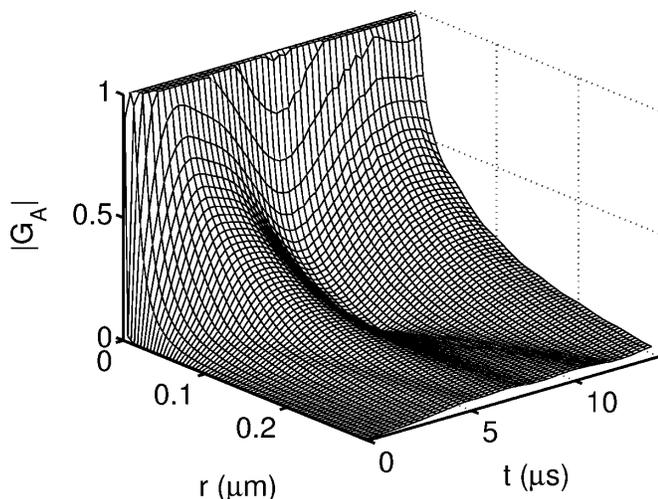
In Fig. 3, we illustrate the behavior of the normal component during this simulation. The density of the normal gas is $G_N(r)|_{r=0}$. The temperature of the normal gas is found from the spatial scale over which this correlation function decays. For reference, for an equilibrium classical gas, G_N is Gaussian with a standard deviation given by the thermal de Broglie wavelength.

In Fig. 4, we show the evolution of the anomalous fluctuations. For a dilute gas, the magnitude of the pair-correlation function is usually small, so it is significant that here $|G_A|$ acquires a large value comparable to that of $|G_N|$. One of the reasons for this behavior is that there can never be an odd number of atoms in the thermal cloud since atoms are spontaneously generated from molecules in pairs. This situation is similar to the formation of a squeezed vacuum in optics. Note that the value of $|G_A(r)|$ near $r = 0$ depends on σ_r^{-1} and is not an observable.

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FIG. 4. Evolution of the anomalous density.