Quantum Superchemistry: Dynamical Quantum Effects in Coupled Atomic and Molecular Bose-Einstein Condensates

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We show that in certain parameter regimes there is a macroscopic dynamical breakdown of the Gross-Pitaevskii equation. Stochastic field equations for coupled atomic and molecular condensates are derived using the functional positive-P representation. These equations describe the full quantum state of the coupled condensates and include the commonly used Gross-Pitaevskii equation as the noiseless limit. The full quantum theory includes the spontaneous processes which will become significant when the atomic population is low. The experimental signature of the quantum effects will be the time scale of the revival of the atomic population after a near total conversion to the molecular condensate.

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Systems which can be described only by a quantum field theory (QFT) are of immense interest in physics at all scales from condensed matter to cosmology [1] but tend to be difficult to investigate either in theory or practice. We analyze a nonlinear, experimentally accessible system which requires a QFT description. There has been much interest recently in the production of a molecular Bose-Einstein condensate (MBEC) from the photoassociation of an atomic Bose-Einstein condensate (BEC) of a weakly interacting dilute gas [2–13]. This process not only produces a new species of BEC but does it through a nonlinear coupling which allows the possibility of quantum statistical effects becoming evident in the dynamics. In this Letter we use the functional positive-P representation to calculate the full quantum dynamics of the atomic and molecular fields, and we show that in certain parameter regimes the Gross-Pitaevskii equation (GPE) can give incorrect results, even for the atomic and molecular populations.

The GPE [14] has been widely successful in describing the dynamical features of weakly interacting dilute gas Bose-Einstein condensates. It includes the effects of s-wave interactions and can be readily generalized to include multicomponent condensates with interspecies couplings [4,15]. As a semiclassical, mean-field theory, it necessarily cannot give information about the quantum statistics of the condensates, but for most experiments with BEC these properties have not been observable. This is not surprising, particularly considering the effectiveness of the semiclassical approximation in quantum optics [16]. One of the simplest systems in quantum optics in which easily observable experimental features depend on the quantum statistics is second harmonic generation, where pairs of photons are coupled to single, high-energy photons [17]. The analogous process in atom optics is that of the coupling of a MBEC and a BEC, which may be done either through tuning of a Feshbach resonance [11] or through photoassociation via a two-photon Raman coupling [4–6].

The Bose enhancement of the photoassociation of atoms from a trapped BEC leads to giant, collective oscillations between the atomic and molecular populations. This enhancement of a chemical process was dubbed "superchemistry" by Heinzen *et al.* when they first modeled it using a two-component Gross-Pitaevskii equation [4]. A more recent model using the Hartree-Fock-Bogoliubov method includes pair correlations in the atomic field and showed discrepancies with the results obtained with the GPE [11]. To investigate the full effects of the quantum nature of the fields, we develop a set of stochastic equations for the atomic and molecular fields based on the functional positive-P representation [18]. The GPE is simply the resulting stochastic partial differential equations with the noise terms removed. The dynamical statistical properties of a BEC have been examined using stochastic differential equations in the positive-P and Wigner representations [19–21], with success limited by the tendency for the individual trajectories to diverge for many physically interesting parameter regimes.

We describe the process of two-color Raman photoassociation by considering a single electronic level for the atomic field and a two-component field for the molecules. The three modes are in a lambda configuration as shown in Fig. 1, with state $|1\rangle$ being the atomic BEC, state $|2\rangle$ the excited state of the MBEC, and state $|3\rangle$ the stable

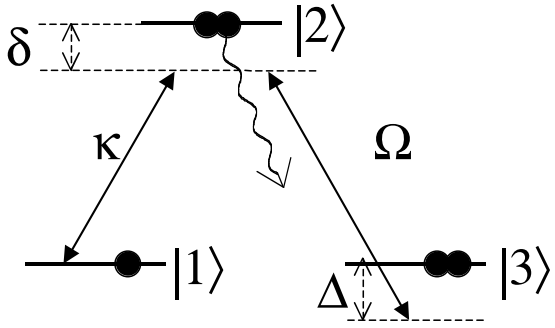

FIG. 1. Energy level scheme for coherent free-bound-bound photoassociation. Levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ are the electronic states for the atomic BEC, the excited MBEC and the stable MBEC respectively.

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MBEC. The excited molecular field is actually composed of multiple vibrational levels, but these excited states are not populated by the Raman transition, so we treat them as a single level which is then adiabatically eliminated. Two separate lasers induce a free-bound coupling between $|1\rangle$ and $|2\rangle$ and a bound-bound coupling between $|2\rangle$ and $|3\rangle$. In a rotating frame, the Hamiltonian may be written as

$$\hat{H} = \sum_{i=1}^{3}\left(\hat{T} + \hat{V}_i + \int dx\, \frac{U_{ii}}{2}\,\hat{\psi}_i^{\dagger 2}(x)\hat{\psi}_i^2(x)\right) + 2i + \frac{i\hbar}{2}\int dx[\kappa(x)\hat{\psi}_1^{\dagger 2}(x)\hat{\psi}_2(x) - \kappa^*(x)\hat{\psi}_1^2(x)\hat{\psi}_2^{\dagger}(x)] + i\hbar\int dx[\Omega(x)\hat{\psi}_2^{\dagger}(x)\hat{\psi}_3(x) - \Omega^*(x)\hat{\psi}_2(x)\hat{\psi}_3^{\dagger}(x)],$$

where $\hat{\psi}_j(x)$ is the field annihilation operator for the atomic or molecular field in state $|j\rangle$, $\hat{T}_i$ and $\hat{V}_i$ are, respectively, the kinetic and potential energy operators for the ith field, U_{kk} is the strength of the interatomic interactions between particles in state $|k\rangle$, $\kappa(x)$ is the Rabi frequency of the free-bound photoassociation, and $\Omega(x)$ is the Rabi frequency of the bound-bound transition. We do not include the interactions between the species, as the strengths of these interactions are not known. In this notation, the detunings of the lasers from the bare atomic and molecular energy levels are included in the potential energy terms V_2 and V_3.

In addition to the coherent effects produced by this Hamiltonian, we may include losses from the levels by adding standard loss terms to the master equation. We write this master equation in the functional positive-P representation [19,22]

$$P(\{\psi^\alpha, \psi^\beta\}, \tau) = \rho^{(a)}(\{\hat{\psi}, \hat{\psi}^\dagger\}, \tau)|_{\hat{\psi}\leftrightarrow\psi^\alpha, \hat{\psi}^\dagger\leftrightarrow\psi^\beta}, \quad (1)$$

where $\rho^{(a)}$ is the density operator antinormally ordered with respect to the field operators in the Schrödinger picture. We may then use the functional operator correspondences,

$$\hat{\psi}\rho \leftrightarrow \psi^\alpha P, \qquad \hat{\psi}^\dagger\rho \leftrightarrow \left(\psi^\beta - \frac{\partial}{\partial\psi^\alpha}\right)P,$$
$$\rho\hat{\psi}^\dagger \leftrightarrow \psi^\beta P, \qquad \rho\hat{\psi} \leftrightarrow \left(\psi^\alpha - \frac{\partial}{\partial\psi^\beta}\right)P, \quad (2)$$

to write a functional Fokker-Planck equation (FPE) from the master equation. This FPE may be written in the form

$$\frac{\partial P}{\partial t} = \sum_\nu \int dx\left[-\partial_\nu A^\nu + \sum_\mu \frac{1}{2}\,\partial_\mu\partial_\nu D^{\mu\nu}\right]P, \quad (3)$$

where the elements μ and ν correspond to the six components of the fields in the positive-P representation: $\{\psi_1^\alpha, \psi_1^\beta, \psi_2^\alpha, \psi_2^\beta, \psi_3^\alpha, \psi_3^\beta\}$, A is the drift vector, D is the diffusion matrix, and $\partial_{(\nu\leftrightarrow\{n,\gamma\})} \equiv \frac{\partial}{\partial\psi_n^\gamma}$. The drift vector is given by

$$A = \begin{pmatrix} \mathcal{K}_1\psi_1^\alpha - i\Gamma_{11}\psi_1^\beta\psi_1^{\alpha 2} + \kappa\psi_1^\beta\psi_2^\alpha \\ -\mathcal{K}_1\psi_1^\beta + i\Gamma_{11}\psi_1^{\beta 2}\psi_1^\alpha + \kappa^*\psi_1^\alpha\psi_2^\beta \\ \mathcal{K}_2\psi_2^\alpha - i\Gamma_{22}\psi_2^\beta\psi_2^{\alpha 2} - \frac{\kappa^*}{2}\psi_1^{\alpha 2} + \Omega\psi_3^\alpha - \frac{\gamma}{2}\psi_2^\alpha \\ -\mathcal{K}_2\psi_2^\beta + i\Gamma_{22}\psi_2^{\beta 2}\psi_2^\alpha - \frac{\kappa}{2}\psi_1^{\beta 2} + \Omega^*\psi_3^\beta - \frac{\gamma}{2}\psi_2^\beta \\ \mathcal{K}_3\psi_3^\alpha - i\Gamma_{33}\psi_3^\beta\psi_3^{\alpha 2} - \Omega^*\psi_2^\alpha \\ -\mathcal{K}_3\psi_3^\alpha + i\Gamma_{33}\psi_3^{\beta 2}\psi_3^\alpha - \Omega\psi_2^\beta \end{pmatrix},$$

where $\mathcal{K}_j = -i/\hbar(\hat{T}_j + \hat{V}_j)$, $\Gamma_{jj} = U_{jj}/\hbar$, and the damping rate of the excited molecular field is γ. The diffusion matrix D is diagonal, with diagonal elements from the vector $B_{\rm sqr}$:

$$B_{\rm sqr} = \{-i\Gamma_{11}\psi_1^{\alpha 2} + \kappa\psi_2^\alpha, i\Gamma_{11}\psi_1^{\beta 2} + \kappa^*\psi_2^\beta, -i\Gamma_{22}\psi_2^{\alpha 2}, i\Gamma_{22}\psi_2^{\beta 2}, -i\Gamma_{33}\psi_3^{\alpha 2}, i\Gamma_{33}\psi_3^{\beta 2}\}.$$

This simple form for the Fokker-Planck equation leads to the following set of Itô stochastic field equations:

$$\frac{\partial\psi_\nu}{\partial t} = A^\nu + \sqrt{B_{\rm sqr}^\nu}\,\eta_\nu, \quad (4)$$

where η_ν are a set of real, Gaussian noise sources which are δ correlated in time and space:

$$\eta_i(x,t)\eta_j(x',t') = \delta_{ij}\delta(x - x')\delta(t - t').$$

These stochastic equations allow us to generate any normally ordered quantum field averages by averaging selected moments of these fields over a sufficiently large sample of trajectories [19]. These equations reduce to the GPE for this system if we ignore the noise terms.

In order for two lasers to provide a two-photon transition without populating the excited MBEC, the single-photon detuning δ must be made very large. This allows us to adiabatically eliminate the upper level. This is equivalent to assuming that the population of the excited level is very small and that its time derivative can be ignored. We assume that we can ignore the terms $\partial_t\psi_2^{\alpha,\beta}(x,t)$, $\hat{T}\psi_2^{\alpha,\beta}$, and $\Gamma_{22}\psi_2^\beta\psi_2^\alpha$ in the equations of motion for $\psi_2^{\alpha,\beta}(x,t)$ as they are smaller than the other terms. This allows us to write solutions for $\psi_2^{\alpha,\beta}(x,t)$ explicitly in terms of $\psi_1^{\alpha,\beta}(x,t)$ and $\psi_3^{\alpha,\beta}(x,t)$ and replace them in Eq. (4) to give a set of equations of motion for the four remaining fields. If we make the adiabatic approximation even stronger and assume that the single-photon detuning δ is larger than the noise terms $\sqrt{\Gamma_{22}}\,\eta_{3,4}$, the excited state loss rate γ, and the trapping potential ($V_2 = \hbar\delta$), then the

resulting equations of motion in scaled units are

$$\begin{aligned}
\frac{\partial\psi_1^\alpha}{\partial\tau} &= \tilde{\mathcal{K}}_1\psi_1^\alpha - i\Gamma_{\rm eff}\psi_1^\beta\psi_1^{\alpha 2} - i\psi_1^\beta\psi_3^\alpha \\
&\quad + \sqrt{-i(\Gamma_{\rm eff}\psi_1^{\alpha 2} + \psi_3^\alpha)}\,\eta_1\,, \\
\frac{\partial\psi_1^\beta}{\partial\tau} &= -\tilde{\mathcal{K}}_1\psi_1^\beta + i\Gamma_{\rm eff}\psi_1^{\beta 2}\psi_1^\alpha + i\psi_1^\alpha\psi_3^\beta \\
&\quad + \sqrt{i(\Gamma_{\rm eff}\psi_1^{\beta 2} + \psi_3^\beta)}\,\eta_2\,, \\
\frac{\partial\psi_3^\alpha}{\partial\tau} &= \tilde{\mathcal{K}}_3\psi_3^\alpha - i\tilde{\Gamma}_{33}\psi_3^\beta\psi_3^{\alpha 2} - \frac{i}{2}\psi_1^{\alpha 2} \\
&\quad + i\frac{\Omega}{\kappa^*}\psi_3^\alpha + \sqrt{-i\tilde{\Gamma}_{33}}\,\psi_3^\alpha\eta_3\,, \\
\frac{\partial\psi_3^\beta}{\partial\tau} &= -\tilde{\mathcal{K}}_3\psi_3^\beta + i\tilde{\Gamma}_{33}\psi_3^{\beta 2}\psi_3^\alpha + \frac{i}{2}\psi_1^{\beta 2} \\
&\quad - i\frac{\Omega^*}{\kappa}\psi_3^\beta + \sqrt{i\tilde{\Gamma}_{33}}\,\psi_3^\beta\eta_4\,,
\end{aligned} \tag{5}$$

where $\chi = \kappa\Omega/\delta$, τ is the scaled time $\tau = \chi t$, $\tilde{\mathcal{K}}_j = \mathcal{K}_j/\chi$, $\tilde{\Gamma}_{jj} = \Gamma_{jj}/\chi$, and $\Gamma_{\rm eff} = \tilde{\Gamma}_{11} - \frac{\kappa}{2\Omega^*}$. Only four noise sources are required in this approximation. To ensure that the adiabatic approximation is being made self-consistently, the density of atoms in the excited state (which must remain small) can be calculated from the amplitudes of the other fields.

This equation of motion is very similar to that obtainable by a direct coupling between the BEC and the stable MBEC, except for the nonlinear light shift of the BEC which is proportional to κ/Ω and the linear light shift of the MBEC which is proportional to Ω/κ. By carefully selecting the ratio of the two laser intensities, the nonlinear light shift can actually cancel the repulsive interactions between the atoms in the BEC. A suitable choice of the two-photon detuning Δ can make the coupling between the two stable species resonant.

The semiclassical approximation has been shown to give incorrect predictions for the mean behavior of the fields in traveling-wave second harmonic generation [17], as well as for their quantum statistical properties [23,24]. This discrepancy is most pronounced when there is nearly complete conversion to the second harmonic, which occurs when the third order nonlinearities are very small [25]. We can examine the same parameter regime for conversion of a BEC to an MBEC by considering a two-photon resonant coupling ($\Delta = |\Omega|^2/\delta$) with very weak third order nonlinearities. The terms proportional to ψ^3 can be made small by considering spatially large traps with moderate particle number. For the atomic BEC, this term can be virtually eliminated by choosing $\tilde{\Gamma}_{11} \approx \frac{\kappa^*}{2\Omega}$, as described earlier. The most direct method of achieving resonance is to make the coupling χ as strong as possible, which can be done independently of our other constraints when both Ω and δ are very large. For the equation of motion scaled to this coupling strength, Eq. (5), this simply reduces the size of both the linear and the self-energy terms. In the limit $\chi \to \infty$ these equations would look exactly like resonant second harmonic generation, for which we know the mean-field approximation breaks down [17]. We now examine the difference between the quantum solution and the semiclassical solution allowing for physical constraints such as limited detuning and laser power.

Since the atomic interactions can be balanced by light shifts, the remaining critical parameter is the intermolecular interactions. Unfortunately, the molecule-molecule scattering length has not been experimentally determined and will depend on the particular molecular state. We therefore show our results based on the assumption that the molecular scattering rate is the same as the atomic scattering rate. If it is weaker, then the difference between the positive-P and GPE results will be greater.

It is experimentally difficult to produce large Rabi frequencies for the atom-molecule interaction due to the low Franck-Condon factors, but this does not appear to be a limitation of this system provided large Rabi frequencies can be achieved for the molecule-molecule transition. Figure 2 shows the evolution of the atomic and molecular populations for $\kappa = 0.29\ \mathrm{MHz\,m^{1/2}}$, $\Omega = 10$ GHz, and $\delta = 100\ \Omega$. We use the mass and scattering length of ^{87}Rb for this calculation. Both condensates are in a quasi-1D harmonic trap of frequency $\omega/2\pi = 6.8$ Hz in the axial direction, and $\omega/2\pi = 200$ Hz in the tightly confining transverse directions. This leads to an effective interatomic repulsion of $\Gamma_{11} = 0.042$ in the one dimensional limit [19].

In a numerical simulation on a spatial grid of cell size Δx and a step size of Δt, the noise terms $\eta(x,t)$ are included at each time step by choosing a random number R from a Gaussian distribution centered around zero and with unit width. We then use $\eta(x,t) = R/\sqrt{\Delta x\Delta t}$. The

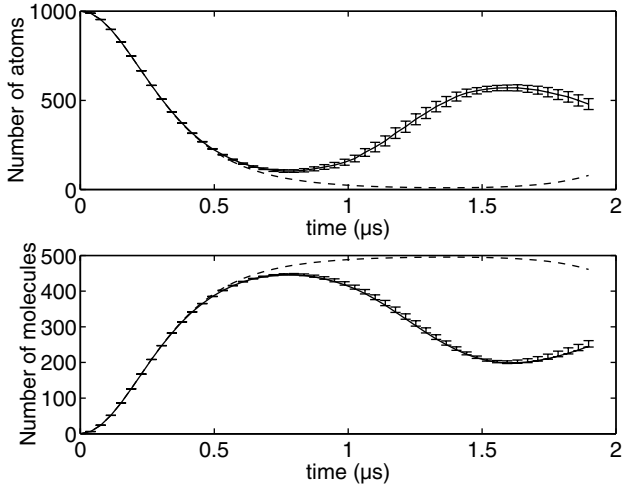

FIG. 2. Atomic and molecular populations for $\chi = 2900\ \mathrm{Hz\,m^{1/2}}$, with $\Gamma_{33} = \Gamma_{11}$. The solid line is the result of the positive-P calculation and the dashed line is the solution of the GPE. The error bars on the positive-P solution are due to the sampling error.

stochastic integration was performed with the XMDS package [26].

Although the GPE solution exhibits a revival in atomic population after this regime, we can see that it is clearly inadequate for predictions over this time scale. The positive-P solution has a sampling error which can be reduced arbitrarily, given a sufficient number of trajectories.

The GPE fails in this example for a relatively simple reason. Let us consider the process of molecular dissociation, which occurs when we begin with a sample of molecules rather than a sample of atoms and use the same Raman transition. The GPE predicts that nothing will happen. This is because it does not contain the spontaneous component of the process, which comes into the full quantum solution through the noise terms. Whenever the system approaches a state in which there are molecules and very few atoms, its evolution will diverge from that of the GPE, which contains only the stimulated processes.

The positive-P representation contains the full description of the quantum field. It therefore includes all quantum statistical effects such as the pair-correlation effects as described by Holland *et al.* [11]. However, the positive-P method cannot be applied to every system of coupled BECs. This is because the individual trajectories, which individually do not have to behave in a physical fashion, can become unstable over time in the absence of damping. The method was successful in this Letter because the interesting physics occurred in early times while the stochastic integration remained stable. These difficulties are partially due to the fact that the coherent state basis which underlies the description is not a natural state of the atomic field, although it is often a good basis for the optical field. It may therefore be advantageous to develop other phase-space representations in order to deal with fully quantum atomic fields in an efficient manner.

Although it has been very successful, the GPE cannot be applied to every system of coupled BECs. While it may seem reasonable to expect that the quantum statistics will tend to affect the multitime correlations of the field rather than the mean field, our result here shows it is also important to include them when considering the equations of motion for moments of the mean field. The signature of the breakdown of the GPE occurs in the simplest experimental observable—the total atomic and molecular populations.

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