Quantum metrology with ultracold chemical reactions

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Chemical chain reactions are known to enable extremely sensitive detection schemes in chemical, biological, and medical analysis, and have even been used in the search for dark matter. Here we show that coherent, ultracold chemical reactions harbor great potential for quantum metrology: In an atom-molecule Bose-Einstein condensate (BEC), a weak external perturbation can modify the reaction dynamics and lead to the coherent creation of molecules in an atom-dominant regime, which can be selectively detected with modern spectroscopic techniques. This promises to substantially improve the viability of previously proposed BEC-based sensors for acceleration, gravitational waves, and other physical quantities, including the detection of dark matter, that so far relied on the detection of the tiny density modulations caused by the creation of single phonons.

Chemical chain reactions, such as the polymerase chain reaction that has become popular in COVID-19 tests, have developed to one of the most important, highly sensitive analysis and detection schemes not only in medicine, but more generally in biological and chemical analysis [1]. Within physics, a “DNA detector” for dark matter particles was proposed [2, 3]. However, the potential of ultracold coherent chemical reactions for quantum metrology has not been studied so far.

The conventional picture of chemical reactions being due to (classical) collisions gets modified drastically at ultralow temperatures. Specifically, when bosonic atoms and molecules lose their individual character and condense in coherent matter waves [4–7], chemical reactions can lead to coherent macroscopic, non-linear oscillatory dynamics even for simple reactions such as \( A + A \rightarrow A_2 \) for which no classical chemical oscillations are possible. Such a collectively enhanced “superchemistry” was demonstrated experimentally by coherent Rabi oscillations between atomic and molecular fields driven by magnetic Feshbach resonances or Raman transitions [8]. The collective chemical reactions of bosonic matter fields lead to a novel type of quasiparticle, which we coin the reacton. It is analogous to phonons in single-component BECs, but represents an elementary excitation of a quantized time- and space-dependent chemical reaction field with vector character that fully describes the reaction dynamics, rather than a single scalar density perturbation.

Its composition in terms of atomic and molecular amplitudes and the corresponding holes can be largely tuned through system parameters.

In what follows, we show that in this regime counting individual molecules facilitates the detection of small perturbations applied to the ultracold gas. We demonstrate that a lower bound of the classical Fisher information from counting molecules approaches the quantum Fisher information which sets the upper bound on the sensitivity with which the perturbation parameter can be estimated [9–11]. Corresponding sensors have been proposed e.g. for measuring acceleration [12], the detection of gravitational waves (GW) [13–16], for gravimeters and measuring the gravitational field gradient on a millimetre scale [17], and the detection of dark matter [18]. However, the classical Fisher information for specific and realizable measurements, and hence the sensitivity in practical realizations for these proposals, is unknown so far. Only the theoretically achievable maximum sensitivity based on the quantum Fisher information (QFI) was established. Ultimately, these proposed sensors require measuring density modulations from a small number of phonons in a BEC, but single phonon detection in condensates has been achieved experimentally so far only in the superfluid helium II [19] and there is no report of achieving single phonon detection in BECs yet. Since, on the other hand, molecules in a BEC can be detected on a single-particle level with spectroscopic techniques [20, 21] (the coherent formation of single molecules was demonstrated in [22]), our scheme presents an important step forward towards the realization of quantum sensors based on density perturbations in a condensate.

Molecular condensates were demonstrated experimentally via magnetic Feshbach resonances and photoassociation [23–25], and coherent oscillations between atomic and molecular condensates were observed [26–28]. Effective quantum field theories were proposed [6, 29, 32] for photoassociation and direct reactions, leading to predictions of non-linear effects known from non-linear optics such as solitons [6] and classical wave chaos [33].

To set the stage of our analysis, we first develop the full quantum field theory of ultracold chemical reactions. Most calculations are delegated to the Supplemental Material.

Quantized chemical reactions

In the Heisenberg picture, the reaction \( A + A \rightarrow A_2 \) of two ultracold bosonic atoms \( A \) in a condensate to an
ultracold bosonic molecule $A_2$ is described in quantum field theory by the Hamiltonian [29 30 32]

$$
\hat{H} = \int d^3r \hat{\psi}^\dagger_a(r,t) \left\{ -\frac{\hbar^2}{2m_a} \nabla^2 + V_a(r,t) \right\} \hat{\psi}_a(r,t) + \frac{g_a}{2} \int d^3r \hat{\psi}^\dagger_a(r,t) \hat{\psi}^\dagger_\bar{a}(r,t) \hat{\psi}_\bar{a}(r,t) \hat{\psi}_a(r,t) \\
+ \frac{g_m}{2} \int d^3r \hat{\psi}^\dagger_m(r,t) \hat{\psi}^\dagger_\bar{m}(r,t) \hat{\psi}_\bar{m}(r,t) \hat{\psi}_m(r,t) \\
+ g_{am} \int d^3r \hat{\psi}^\dagger_a(r,t) \hat{\psi}^\dagger_m(r,t) \hat{\psi}_m(r,t) \hat{\psi}_a(r,t) + h.c. \right\},
$$

where we have normalized the couplings as follows, 

$\tilde{g}_{am} := \frac{g_{am}}{g_a}, \tilde{g}_m := \frac{g_m}{g_a}, \tilde{c} := \frac{\alpha \sqrt{2\hbar}}{g_a n},$ 

and $\varphi_m(t) := \varphi_m(t) - 2\varphi_a(t)$, $x(t) := |\psi_a(t)| / \sqrt{m}$, and $y(t) := |\psi_m(t)| / \sqrt{m}$. Note that Eq. (3) is minimized for

$$
\alpha \cos \varphi_{am}(t) = - |\alpha| \text{ since } x^2(t) \geq 0.
$$

We use below in [5] a Bogoliubov expansion to go beyond mean field theory. In order to not mask the effects of the time-dependent perturbation (whose amplitude we want to probe), by a time-dependent mean-field background, we impose vanishing mean-field Josephson oscillations between atoms and molecules [30] (cf. Eq. (54) in the Supplement). This can be achieved as follows: From Eq. (50), $\varphi_{am}(t)$ can be set to be a constant, and hence, when $\alpha \cos \varphi_{am}(t) = - |\alpha|$, from Eq. (55), $x(t)$ and $y(t)$ are also constant in time. Rendering $\varphi_{am}(t)$ constant in time with $\alpha \cos \varphi_{am} = - |\alpha|$ is possible by tuning $\tilde{c}$ to

$$
\tilde{c} = 2x^2 + \tilde{g}_m (2y^2 - x^2) - \tilde{g}_m y^2 - \frac{|\alpha|}{4 y} \left( 4y - \frac{x^2}{y} \right).
$$

Then $\varphi_a(t)$ and $\varphi_m(t)$ become constant in time, and by minimizing $H_0 - \mu N$, $x$ and $y$ follow from Eq. (512) and $x = \sqrt{1 - 2y^2}$ from Eq. (2) (see supplemental material [4] for derivations). For simplicity, we will set $\varphi_a = 0$ and $\tilde{g}_m = 0$ in what follows.

Fig. 1 shows the physical parameter regimes of $\tilde{g}_am$ and $|\bar{\alpha}|$, defined by $x, y \geq 0$, hence $0 \leq y \leq 1 / \sqrt{2}$. We focus on the atom-dominated case, so for $\tilde{g}_am > 1$, we choose $y_3$, the third solution of Eq. (512). For $\tilde{g}_am < 0$, Fig. 1 shows that only the first solution $y_1$ of Eq. (512) is physical and hence we choose that one.

### Quasiparticle excitations: Reactons

A Bogoliubov expansion [37] of the grand canonical

$$
\tilde{N} := \int d^3r \left\{ \hat{\psi}^\dagger_a(r,t) \hat{\psi}_a(r,t) + 2 \hat{\psi}^\dagger_m(r,t) \hat{\psi}_m(r,t) \right\},
$$

commutes with the Hamiltonian in Eq. (1), is not explicitly time-dependent, and hence conserved; we denote by $\tilde{N}$ the average value of $\tilde{N}$.

### Mean-field description

We expand $\psi_j(r,t) = \psi_j(r,t) + \delta \psi_j(r,t)$ where

$$
\psi_j(r,t) := \langle \psi_j(r,t) \rangle \text{ is the mean-field value of } \hat{\psi}_j(r,t)
$$

for $j = a, m$, for small corrections $\delta \hat{\psi}_j(r,t) \ll \psi_j(r,t)$ where most of atoms and molecules are condensed, respectively. For a box trap [34], where $V_a(r,t) = 0$ and $V_m(r,t) = 0$, let $V$ be the system volume and $n := V / N$ the total number density. $\psi_a(r,t) = |\psi_a(t)| \exp[i \{ \varphi_a(t) - \mu t / \hbar \}]$ and $\psi_m(r,t) = |\psi_m(t)| \exp[i \{ \varphi_m(t) - 2\mu t / \hbar \}]$ satisfy the mean field Eqs. (54) and (55), and the mean-field Hamiltonian $H_0$ reads

$$
H_0 \left( t / (Ng_a) \right) = \frac{1}{2} x^4(t) + \frac{1}{2} \tilde{g}_m y^4(t) + \tilde{c} y^2(t) + \tilde{g}_am x^2(t) y^2(t) + \tilde{\alpha} x^2(t) y(t) \cos \varphi_{am}(t),
$$

where

- $y_1$ is the physical value of $y$, whereas for $\tilde{g}_am > 1$, $y_2$ or $y_3$ are physical values of $y$.
- In the gray zones, no physical solution of $y$ exists (upper zone: $y > 1 / \sqrt{2}$ and $x$ is imaginary; lower zone: no real solutions $x$ and $y$ exist). The orange plane is a projection of the physical values of $y_1$.

![Figure 1](image-url)
Hamiltonian corresponding to in Fourier space gives (up to \( O \left( \delta \hat{\Psi}^2 \right) \))

\[
\hat{H} - \mu \hat{N} = H_0 - \mu N - \frac{g_{nn}}{2} \sum_{k \neq 0} \{ M_{11}(k) + M_{22}(k) \}
+ \frac{g_{nn}}{2} \sum_{p, q, r, k \neq 0} \left[ \hat{\omega}_p(k) \hat{b}_p^\dagger(k, t) \hat{b}_p(k, t)
+ \hat{\omega}_p^*(k) \hat{b}_p^\dagger(-k, t) \hat{b}_p^\dagger(-k, t) \right],
\]

where \( \hat{\omega}_p(k) := \hat{\omega}_p(k) / (g_{nn}) \), \( \hat{\omega}_p^*(k) \) is the complex conjugate of \( \hat{\omega}_p(k) \), and we label \( p = 1,2 \) such that \( \text{Re} \{ \omega_1(0) \} \geq \text{Re} \{ \omega_2(0) \} \). Note that Eq. (5) gives \( \hat{b}_p(k, t) = \exp[-i \text{Re} \{ \omega_p(k) \} t] \hat{b}_p(k, 0) \), which shows that our Bogoliubov Hamiltonian in Eq. (5) is constant in time \( t \).

The \( \hat{b}_p(k, t) \) are bosonic annihilation operators of the \( p \)th Bogoliubov mode (\( p = 1,2 \)), i.e. linear combinations of the Fourier transforms of \( \delta \hat{\phi}_\alpha(r, t) \) and \( \delta \hat{\psi}_m(r, t) \) and their hermitian conjugates via Eq. |S20|. These linear combinations are “reaction fields” whose time-evolution due to the coherent, collective chemical reactions determines the dynamics of the spatiotemporal dependence of the atomic and molecular concentrations. The \( \hat{b}_p(k, t) \) describe quantized excitations of the reaction fields, and \( M_{11}(k), M_{22}(k) \) are defined in Eqs. |S16| and |S17|.

The dimensionless eigenvalues \( \hat{\omega}_p(k) \) of the \( p \)th Bogoliubov mode define the two dispersion branches of reactions. They come in pairs of opposite signs, where, however, only the positive-frequency branches are physically meaningful |37|. We additionally define the dimensionless gap \( \Delta \hat{\omega}(0) := \hat{\omega}_2(0) - \hat{\omega}_1(0) \) for convenience.

Using the approach of |36| facilitates analytic expressions for \( \hat{\omega}_p(k) \) in Eqs. |S47|. We find that \( \hat{\omega}_p(k) \) depends on \( |\alpha| \), and expand \( \hat{\omega}_p(k) \) up to \( O(k^2) \) in Eqs. |S59| to |S58|:

1. \( \hat{\omega}_1(0) \) becomes imaginary if \( A_1 < 0 \).
2. \( \hat{\omega}_1(k) = k \sqrt{\alpha} \sqrt{B_2 - B_3/4A_1} \). Thus, if \( B_2 - B_3/4A_1 < 0 \), \( \hat{\omega}_1(k) \) becomes purely imaginary.

Fig 2(a) shows the gap \( \Delta \hat{\omega}(0) \), where grey regions represent that the gap has nonzero imaginary value and black regions that \( \hat{\omega}_1(k) \) becomes imaginary. In both regions, the system is unstable and we will thus exclude them.

Sources of damping for collective excitations in single-component BECs are Landau damping, which is dominant at higher temperatures and is \( \propto k_B T \) for \( k_B T \gg m_c^2 \), and Beliaev damping at lower temperatures (\( k_B T \ll m_c^2 \)) and if \( h \kappa \ll m_c \) |35|. For \( h \kappa \ll m_c \) linear in \( \kappa \) (corresponding to Nambu-Goldstone modes), in a large range, Landau and Beliaev dissipation and quasiparticle damping are negligible |39|. We will focus on an atom-rich regime, and hence expect that these damping mechanisms can also be neglected in our system.

For \( \omega_1(k) \in \mathbb{R} \), since \( i \partial \hat{b}_1(k, t) / \partial t = \omega_1(k) \hat{b}_1(k, t) \), from Eq. (5), if \( \omega_1(k) = c_r + O(k^2) \), we have \( k^2 \hat{b}_1(k, t) + \left( 1/c_r^2 \right) \partial^2 \hat{b}_1(k, t) / \partial t^2 = O(k^3) \), which is a wave equation for \( \hat{b}_1(k, t) \) in the small \( k \) limit, with the reaction propagation speed \( c_r \). We have \( c_r = (\xi_s g_{nn} / \hbar) \sqrt{B_2 - B_3/4A_1} \) = \( \sqrt{B_2 - B_3} / (4A_1) \sqrt{g_{nn} / (2m_a)} \), which leads to \( c_r / c_s = \sqrt{(B_2 - B_3) / (4A_1)} / 2 \) shown in Fig. 2(b).

Since our Hamiltonian in Eq. (5) is constant in time, from the Bogoliubov expansion in Eq. (S20), using the notation of Eq. |S31|, the annihilation operator for reaction branch \( p \) can be decomposed as

\[
\hat{b}_p(k, t) = u_{p1}(k) \delta \hat{\psi}_m(k, t) - v_{p1}(k) \delta \hat{\psi}_m^\dagger(-k, t)
+ u_{p2}(k) \delta \hat{\psi}_m(k, t) - v_{p2}(k) \delta \hat{\psi}_m^\dagger(-k, t),
\]

We define a cutoff \( k_c \) and choose parameters \( \tilde{g}_{am} \) and \( \alpha \) such that \( \omega_1(k) \ll \omega_2(0) \) for \( k < k_c \), implying that excitations of the second reaction branch can be neglected, and such that for \( k > k_c \), \( \omega_1(k) \rightarrow 0 \). Then in summations involving \( \omega_1(k) \) or \( \omega_2(k) \) over all \( k \), the effect of the massive reacton branch is negligible. From now on, we set for concreteness \( \tilde{g}_{am} = 100 \) and \( \alpha = 1 \) where \( \omega_1(k_c) = 0.1 \omega_2(0) = 19.6 \) with \( k_{c4} = 4.32 \). Then the mean-field state is an “atom-rich” state as \( y^2 = 6.5 \times 10^{-6} \). For these and \( \phi_{am} = 0 \) and \( \alpha \cos \phi_{am} = -|\alpha| \), the eigenvectors \( \{ u_{p1}(k), u_{p2}(k), v_{p1}(k), v_{p2}(k) \} \) are all real.

Fig 2 shows that for \( k < k_c \), \( \tilde{b}_1 \) is more “atomic” in the sense that the coefficient of \( \delta \hat{\psi}_m \) is bigger than that of \( \delta \hat{\psi}_m \), i.e. also in the reaction excitations atoms

![FIG. 2.](image-url)
dominate over molecules. Also, \( u_{1q}(k) \simeq -v_{1q}(k) \) for \( q = 1, 2 \), which means that \( \hat{b}_1 \) has approximate particle-hole symmetry near \( k = 0 \) as for a single-component BEC.

In the Supplement [11] we show that creation and annihilation of pairs of reactons, \( \hat{b}_1^\dagger(\mathbf{k}, t) \hat{b}_1^\dagger(-\mathbf{k}, t) \) and \( \hat{b}_1(\mathbf{k}, t) \hat{b}_1(-\mathbf{k}, t) \) over any nonzero \( \mathbf{k} \) converts atoms to molecules and vice versa. This can be formalized in a reaction rate operator \( \tilde{R}_2(t) \) defined in Eq. (S97), which shows that \( \alpha \Xi_{13}(k) \) determines the reaction rate, up to the expectation values of \( \hat{b}_1^\dagger(\mathbf{k}, t) \hat{b}_1^\dagger(-\mathbf{k}, t) - h.c. \) that depend on the specific quantum state of the reactons. \( \Xi_{13} \) is defined in (S90). Fig. 1 shows that \( \alpha \Xi_{13}(k) \) is symmetric in \( \tilde{a} \) and its absolute value increases as \( k \) increases. It also increases as one approaches the boundary of the grey regions where \( y \) does not have physical values.

**Metrology with quantized chemical reactions**

We now demonstrate the metrological usefulness of ultracold chemical reactions for which small molecule concentrations can be detected [21]. To that end, we compare a lower bound of the classical Fisher information (CFI) based on molecule counting with the quantum Fisher information (QFI) for various small, time-dependent perturbations \( \hat{V}(t) \) turned on at time \( t = 0 \). As until \( t = 0 \) our Hamiltonian is time-independent (see Eq. (5)), we use the interaction picture with state \( |\Psi_I(t)\rangle \) and initial state \( |\Psi_I(0)\rangle = |\text{vac}\rangle \) to calculate the response to \( \hat{V}(t) \). Here, \( |\text{vac}\rangle \) is the Bogoliubov vacuum, \( \hat{b}_1^\dagger(\mathbf{k}, t \leq 0) |\text{vac}\rangle = 0 \), and \( \hat{b}_1^\dagger(\mathbf{k}, t) \) are the Bogoliubov operators in the interaction picture. Hence, before time-dependent perturbations are applied, the system has lowest energy up to \( O(\delta \tilde{\Psi}_j^3) \) (see Eq. (5)).

We calculate the QFI and a lower bound to the CFI derived in [40], for details see the Supplement [IV]. The inverse of the QFI defines the smallest uncertainty with which a parameter can be estimated, optimized over all possible ("positive operator-valued measure", POVM) measurements and data analysis schemes with unbiased estimators. This so-called quantum Cramér-Rao bound [11][22] can be saturated in the limit of a large number of measurements and hence constitutes an important fundamental benchmark for the sensitivity with which a parameter can be estimated that is in principle achievable once all technical noise has been eliminated and only noise inherent in the quantum state remains. While our scheme is general, we illustrate it at the hand of one example: the amplitude of a metric perturbation that arises e.g. from a gravitational wave on top of a flat Minkowski space-time background.

A metric perturbation \( h_{\xi\xi}(\xi, \eta, \zeta, t) \) on top of a flat Minkowski spacetime, created by a gravitational wave propagating in \( \zeta \)-direction, leads to a Newtonian tidal force in \( \xi \) direction on non-relativistic particles of mass \( m \) given by (see Eq. (8.2) in [32]) \( F_\xi = (m/2)\tilde{h}_{\xi\xi} \), where \( h \) is in transverse traceless gauge, \( r = (\xi, \eta, \zeta) \) and time \( t \) are coordinates in the proper detector frame of a free-falling observer, and a dot signifies time-derivative. In the simplest mono-chromatic case, \( h_{\xi\xi} = h_{\xi\xi} \sin(k_\xi \zeta - \omega_{GW} t) \). The force derives from a potential \( \tilde{U} = -(m/4)\xi^2 h_{\xi\xi} \), which translates to an interaction hamiltonian between the GW and the BEC located at \( \zeta = 0 \) given in second quantization by \( \tilde{V}_S(t) \) with

\[
\frac{L^2 \omega_{GW}^2}{48} \tilde{h}_{\xi\xi} \sin(\omega_{GW} t) \sum_{l=a,m} m_l \sum_{k \neq 0} \delta \tilde{\Psi}_l^\dagger(\mathbf{k}) \delta \tilde{\psi}_l(\mathbf{k}), \tag{7}
\]

where we assumed a 1D BEC aligned in \( \xi \) direction, and approximated \((1/L) \int_{-L/2}^{L/2} d\xi e^{i(k_\xi \zeta - k_\xi \zeta L/2)} \approx L^2 \delta k_\xi k_\xi/12\), where \( L \) is the length of the quasi-1D BEC. The latter approximation means that the GW couples purely to mass density and scattering of reactons due to the spatial structure of the GW is neglected on the length-scale of the BEC. The latter approach means that the GW couples purely to mass density and scattering of reactons due to the spatial structure of the GW is neglected on the length-scale of the BEC. The parts linear in \( \delta \tilde{\psi}_l(r, t) \) vanish as we set our background mean-field to be homogeneous in space (i.e. it has only a \( \mathbf{k} = 0 \) component).

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**FIG. 3.** Bogoliubov mode amplitudes in Eq. (4), \( u_{11}(\mathbf{k}) \), \( u_{12}(\mathbf{k}) \), \( -v_{11}(\mathbf{k}) \) (Black line), \( u_{12}(\mathbf{k}) \) (Red dashed), and \( -v_{12}(\mathbf{k}) \) (Blue dashed) as a function of \( k\tilde{a} \) at \( g_{anm} = 100 \) and \( \tilde{a} = 1 \). Inset: \( v_{12} \) (Red dashed) and \( -v_{12} \) (Blue dashed) with \( 0 < k\tilde{a} < 0.001 \). As \( k \to 0 \), \( u_{aq}/(-v_{aq}) \to 1 \), which implies that atomic (or molecular) creation- and annihilation operators contribute equally to \( \tilde{b}_1 \) near \( k = 0 \).

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**FIG. 4.** \( \alpha \Xi_{13}(k) \) which determines reaction rates (see Eqs. (S97), (S98), (S100)) as a function of \( g_{anm} \) and \( \tilde{a} \). Left figure is for \( k = 2\pi/L \), and right figure is for \( k = 20\pi/L \) with parameters in the table (d) of [2] \( y \) does not have physical values in the grey regions.
The perturbation in Eq. (7) applied to the system with box trap potentials satisfies \( V_m(t) = 2V_0(t) \) and hence, from Eqs. (55) and (59), the background mean field remains homogeneous in space. One can write \( \hat{V}_S(t) = Vex f(t) \int d^3r \left\{ \hat{\delta} \psi_k^*(r) \hat{\delta} \psi_k(r) + 2\hat{\delta} \psi_k^*(r) \hat{\delta} \psi_m(r) \right\} \) with \( Vex = -E^2 \omega^2_{GW} \hbar \xi \alpha \) and \( f(t) = \sin(\omega_{GW} t) \). Throughout, we assume that the perturbations are small such that \( Vex \ll \hbar \omega_k(k) \) for \( k \neq 0 \).

A large class of sensing applications, including the one mentioned above, is covered by the following generic perturbation, bilinear in the lower reacton branch basis, which acts on the system from \( t = 0 \):

\[
\hat{V}_S(t) = Vex f(t) \sum_{k \neq 0} V_1(k) \hat{b}_k^\dagger \hat{b}_k \hat{b}_1^\dagger \hat{b}_1
\]

\[
+ Vex f(t) \sum_{k \neq 0} \left\{ V_2(k) \hat{b}_k^\dagger \hat{b}_1^\dagger (-k) + \text{h.c.} \right\}, \quad (8)
\]

where \( Vex, f(t), \) and \( V_1(k) \) are real. \( Vex > 0 \) has units of energy and we define the dimensionless \( Vex := Vex/\langle g_n \rangle \).

Also, for periodic perturbations with angular frequency \( \omega_n \), we set \( \hat{\omega}_n := \hbar \omega_n/\langle g_n \rangle \). We assume \( |f(t)| \leq 1 \forall t \) and focus on a 1D system with parameters given in table (d) in Fig. 2 using values of a \(^{87}\)Rb BEC experiment \(^{11}\) and define \( k_n := 2\pi n/L \) where the summation over \( k \) becomes a summation over integers \( n_1 \). We define the cutoff \( n_c \) such that \( \hat{\omega}_1(k_n) = 0.1\omega_2(0) \) in order not to excite any massive reactions, as this would complicate the dynamics substantially. Since \( k_c \xi_0 = 32, \) the closest integer \( n_c \) is 110 where \( k_n = 4.28, \) which satisfies \( v_{11} \) \( (k_n) \) and \( v_{12} \) \( (k_n) \) \( \rightarrow 0, \) cf. left panel of Fig. 5.

We give the result for the QFI and the CFI based on molecule counting for a general perturbation \(^8\) in Eqs. (57) and (59). In Fig. 5, we show the ratio of the lower bound \( I_C(\hat{t}) \) of the CFI and the QFI \( I_Q(\hat{t}) \) for 6 different temporal perturbation profiles for density perturbations when estimating \( \hat{Vex} \). In the Supplement IV B we show that our QFI calculation for \( t > 1 \) and the perturbation \(^7\) is consistent with \(^{12}\) when there are no BEC molecules in the system. While the functional form of the ratio \( I_C(\hat{t})/I_Q(\hat{t}) \) depends on the form of the signal, the most important message is that CFI and QFI are on the same order of magnitude. Counting molecules therefore constitutes a close-to-optimal measurement for homogeneous density perturbations. This is a central result of this paper that goes beyond previous proposals of sensors based on density perturbations in BECs \(^{12}\) for which so far no practical measurement schemes with corresponding sensitivities were known.

**Conclusion and outlook**

In summary, we explored quantized chemical reactions in ultracold gases of atoms and molecules for their use in quantum metrology. Both the atom/molecule ratio in the mean-field ground state and the composition of the “reacton” quasiparticles, the quantized excitation of the fields that describe the chemical reactions in space and time, can be widely tuned with the parameters of the system. We identified an atom-rich regime, where the mean-field dynamics is shut off, and the creation of molecules dominated by the response to an external perturbation. We showed that a measurement of the number of molecules in this regime is very close to reaching maximum possible sensitivity for perturbations that couple to the total density of atoms (including the molecules).

Since single-molecule counting can be achieved with established spectroscopic techniques, our scheme offers an attractive alternative to proposed quantum metrological schemes that require the detection of single phonons in BECs \(^{13}\) \(^{15}\), which is an extremely challenging task experimentally \(^{16}\) \(^{17}\). With spatially resolved molecule detection one might even be able to identify the modes in which the molecules are created and hence acquire additional information about an external perturbation of the system.

Numerous other avenues of quantum metrology based on ultracold chemistry can be explored, such as the exploration of unstable regions, or more complex reactions. Atomic analogues of superconducting transition-edge detectors \(^{48}\) might be envisaged, and chemical chain reactions in the regime of ultracold quantum gases explored (see also \(^{49}\) for the benefits of chaotic dynamics for metrology). Quantized reaction rates could also be studied on a self-consistent level \(^{50}\), creating an avenue to many-body quantum chemical oscillations and their metrology beyond Bogoliubov theory.

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Author contributions

SHS did main calculations (details in the supplemental material), part of numerical calculations, and made figures.

URF defined major research directions, provided the cold atoms knowledge and Bogoliubov theory background, including (a) the clarification of analogies and differences to two-component BECs (b) established the vanishing mean-field oscillations condition, (c) identified the necessary form of the Bogoliubov spectrum and (d) identified key publications for the Bogoliubov theory of atom-molecule mixtures.

DB conceived the general idea, defined major research directions and identified key publications, co-supervised the research, performed parts of the calculations, and wrote the first version of the manuscript.

All authors discussed all results and the manuscript at all times.

Competing interests

The authors declare no competing interests.

[1] Erik E. Augustus, Muhiy Rana, and Mehmet V. Yigit, “Chemical and Biological Sensing Using Hybridization Chain Reaction,” ACS Sensors 3, 878–902 (2018).
[2] A. K. Drukier, A. C. Cantor, M. L. Chonofsky, G. M. Church, R. L. Fagaly, K. Freese, A. Lopez, T. Sano, C. Savage, and W. P. Wong, “New class of biological detectors for WIMPs,” International Journal of Modern Physics A 29, 1433007 (2014).
[3] Ciaran A. J. O’Hare, Vassili G. Matsos, Joseph Newton, Karl Smith, Joel Hochstetter, Ravi Jaiswar, Wunna Kyaw, Aimee McNamara, Zdenka Kuncic, Sushma Nagaraja Gresleischeid, and Celine Boehm, “Particle detection and tracking with DNA,” arXiv e-prints (2021).
[4] N. Balakrishnan, “Perspective: Ultracold molecules and the dawn of cold controlled chemistry,” The Journal of Chemical Physics 145, 150901 (2016).
[5] Brianna R. Heazlewood and Timothy P. Softley, “Towards chemistry at absolute zero,” Nature Reviews Chemistry 5, 125–140 (2021).
[6] P. D. Drummond, K. V. Kheruntsyan, and H. He, “Coherent Molecular Solitons in Bose-Einstein Condensates,” Phys. Rev. Lett. 81, 3055–3058 (1998).
[7] D. J. Heinzen, Roahn Wynar, P. D. Drummond, and K. V. Kheruntsyan, “Superchemistry: Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates,” Phys. Rev. Lett. 84, 5029–5033 (2000).
[8] Roahn Wynar, R. S. Freeland, D. J. Han, C. Ryu, and D. J. Heinzen, “Molecules in a Bose-Einstein Condensate,” Science 287, 1016–1019 (2000).
[9] C.W. Heistrom, “Minimum mean-squared error of estimates in quantum statistics,” Physics Letters A 25, 101–102 (1967).
[10] Samuel L. Braunstein and Carlton M. Caves, “Statistical distance and the geometry of quantum states,” Phys. Rev. Lett. 72, 3439–3443 (1994).
[11] A. S. Holevo, Probabilistic and Statistical Aspect of Quantum Theory (North-Holland, Amsterdam, 1982).
[12] Mehdi Ahmadi, David Edward Bruschi, and Ivette Fuentes, “Quantum metrology for relativistic quantum fields,” Phys. Rev. D 89, 065028 (2014).
[13] Carlos Sabin, David Edward Bruschi, Mehdi Ahmadi, and Ivette Fuentes, “Phonon creation by gravitational waves,” New Journal of Physics 16, 085003 (2014).
[14] Dennis Rätzel, Richard Howl, Joel Lindkvist, and Ivette Fuentes, “Dynamical response of Bose-Einstein condensates to oscillating gravitational fields,” New Journal of Physics 20, 073044 (2018).
[15] Matthew P.G. Robbins, Niayesh Afshordi, and Robert B. Mann, “Bose-einstein condensates as gravitational wave detectors,” Journal of Cosmology and Astroparticle Physics 2019, 032–032 (2019).
[16] S. Singh, L. A. De Lorenzo, I. Pikovski, and K. C. Schwab, “Detecting continuous gravitational waves with superfluid4He,” New Journal of Physics 19, 075023 (2017), publisher: IOP Publishing.
[17] Tupac Bravo, Dennis Rätzel, and Ivette Fuentes, “Phononic gravity gradiometry with Bose-Einstein condensates,” arXiv:2001.10104 [quant-ph] (2020), arXiv: 2001.10104 version: 2.
[18] Richard Howl and Ivette Fuentes, “Quantum Frequency Interferometry: with applications ranging from gravitational wave detection to dark matter searches,” arXiv:2103.02618 [cond-mat, physics:gr-qc, physics:quant-ph] (2021), arXiv: 2103.02618.
[19] A. B. Shkarin, A. D. Kashkanova, C. D. Brown, S. Garcia, K. Ott, J. Reichel, and J. G. E. Harris, “Quantum Optomechanics in a Liquid,” Phys. Rev. Lett. 122, 153601 (2019).
[20] Kevin M. Jones, Eite Tiesinga, Paul D. Lett, and Paul S. Julienne, “Ultracold photoassociation spectroscopy: Long-range molecules and atomic scattering,” Rev. Mod. Phys. 78, 483–535 (2006).
[21] Chris J. Vale and Martin Zwierlein, “Spectroscopic probes of quantum gases,” Nature Physics 17, 1305–1315 (2021).
[22] Xiaodong He, Kunpeng Wang, Jun Zhuang, Peng Xu, Xiang Gao, Ruijun Guo, Cheng Sheng, Min Liu, Jin Wang, Jiaming Li, G. V. Shlyapnikov, and Mingsheng Zhan, “Coherently forming a single molecule in an optical trap,” Science 370, 1311–1315 (2020).
[23] Thorsten Köbler, Krzysztof Góral, and Paul S. Julienne, “Production of cold molecules via magnetically tunable feshbach resonances,” Rev. Mod. Phys. 78, 1311–1361 (2006).
[24] Kevin M. Jones, Eite Tiesinga, Paul D. Lett, and Paul S. Julienne, “Ultracold photoassociation spectroscopy: Long-range molecules and atomic scattering,”
Elizabeth A. Donley, Neil R. Claussen, Sarah T. Thompson, Yi Yan, B. J. DeSalvo, Ying Huang, P. Naidon, and Marijan Kostur, Matt Mackie, Robin Côté, and Juha Javanainen and Matt Mackie, “Coherent photoassociation of a Bose–Einstein condensate,” Nature 417, 529–533 (2002).

Zhendong Zhang, Liangchao Chen, Kai-Xuan Yao, and Cheng Chin, “Transition from an atomic to a molecular Bose–Einstein condensate,” Nature 592, 708–711 (2021).

Zhendong Zhang, Shu Nagata, Kaixuan Yao, and Cheng Chin, “Many-body Chemical Reactions in a Quantum Degenerate Gas,” (2022), arXiv:2207.08295 [cond-mat, physics:physics, physics:quant-ph].

Juha Javanainen and Matt Mackie, “Coherent photoassociation of a Bose-Einstein condensate,” Phys. Rev. A 59, R3186–R3189 (1999).

Martijn Kostrum, Matt Mackie, Robin Côté, and Juha Javanainen, “Theory of coherent photoassociation of a Bose-Einstein condensate,” Phys. Rev. A 62, 063616 (2000).

Pascal Naidon, Eite Tiesinga, and Paul S. Julienne, “Two-Body Transients in Coupled Atomic-Molecular Bose-Einstein Condensates,” Phys. Rev. Lett. 100, 030401 (2008).

Florian Richter, Daniel Becker, Cédric Bény, Torben A. Schulze, Silke Ospelkaus, and Tobias J. Osborne, “Ultra-cold chemistry and its reaction kinetics,” New Journal of Physics 17, 055005 (2015).

Amit Dey and Amichay Vardi, “Interaction-induced instability and chaos in the photoassociative stimulated Raman adiabatic passage from atomic to molecular Bose-Einstein condensates,” Phys. Rev. A 101, 053627 (2020).

Nir Navon, Robert P. Smith, and Zoran Hadzibabic, “Quantum gases in optical boxes,” Nature Physics 17, 1334–1341 (2021).

Equation numbers in the form (S... refer to equations in the Supplement.

Chi-Yong Lin, E. J. V. de Passos, A. F. R. de Toledo Piza, Da-Shin Lee, and M. S. Hussein, “Bogoliubov theory for mutually coherent hybrid atomic molecular condensates: Quasiparticles and superchemistry,” Phys. Rev. A 73, 013615 (2006).

Yuki Kawaguchi and Masahito Ueda, “Spinor Bose–Einstein condensates,” Physics Reports 520, 253–381 (2012).

Ming-Chiang Chung and Aranya B Bhattacharjee, “Damping in 2D and 3D dilute Bose gases,” New Journal of Physics 11, 123012 (2009).

Kazuma Nagao and Ippei Danshita, “Damping of the Higgs and Nambu-Goldstone modes of superfluid Bose gases at finite temperatures,” Progress of Theoretical and Experimental Physics 2016 (2016), 063601.

Manuel Stein, Amine Mezghani, and Josef A. Nossek, “A Lower Bound for the Fisher Information Measure,” IEEE Signal Processing Letters 21, 796–799 (2014).

C RádhaKrishna Rao, “Information and the accuracy attainable in the estimation of statistical parameters,” Reson. J. Sci. Educ 20, 78–90 (1945).

C. Helstrom, “The minimum variance of estimates in quantum signal detection,” IEEE Transactions on Information Theory 14, 234–242 (1968).

Michele Maggiore, Gravitational waves: Volume 1: Theory and experiments, Vol. 1 (Oxford university press, 2008).

E. A. Burt, R. W. Ghrist, C. J. Myatt, M. J. Holland, E. A. Cornell, and C. E. Wieman, “Coherence, Correlations, and Collisions: What One Learns about Bose-Einstein Condensates from Their Decay,” Phys. Rev. Lett. 79, 337–340 (1997).

Richard Howl, Lucia Hackermüller, David Edward Bruschi, and Ivette Fuentes, “Gravity in the quantum lab,” Advances in Physics: X 3, 1383184 (2018).

Ralf Schützhold, “Interaction of a Bose-Einstein condensate with a gravitational wave,” Phys. Rev. D 98, 105019 (2018).

Dennis Rätzel and Ralf Schützhold, “Decay of quantum sensitivity due to three-body loss in Bose-Einstein condensates,” Phys. Rev. A 103, 063321 (2021).

Joel N Ullom and Douglas A Bennett, “Review of superconducting transition-edge sensors for x-ray and gamma-ray spectroscopy,” Superconductor Science and Technology 28, 084003 (2015).

Lukas J. Fisher and Daniel Braun, “Quantum metrology with quantum-chotic sensors,” Nature Communications 9, 1351 (2018).

Olir E. Alon, Alejx I. Streltsov, and Lorenz S. Cederbaum, “Many-body theory for systems with particle conversion: Extending the multiconfigurational time-dependent Hartree method,” Phys. Rev. A 79, 022503 (2009).

Y. Castin and R. Dum, “Low-temperature bose-einstein condensates in time-dependent traps: Beyond the u(1) symmetry-breaking approach,” Phys. Rev. A 57, 3008–3021 (1998).

C. J. Pethick and H. Smith, Bose-Einstein Condensation in Dilute Gases 2nd ed. (Cambridge University Press, 2008).

Jing Liu, Xiao-Xing Jing, Wei Zhong, and Xiao-Guang Wang, “Quantum Fisher information for density matrices with arbitrary ranks,” Communications in Theoretical Physics 61, 45–50 (2014).

L.P. Pitaevskii, S. Stringari, and Oxford University Press, Bose-Einstein Condensation International Series of Monographs on Physics (Clarendon Press, 2003).

Sofia Qvarfort and Alessio Serafini and André Xuereb and Daniel Braun and Dennis Rätzl and David Edward Bruschi, “Time-evolution of nonlinear optomechanical systems: interplay of mechanical squeezing and non-gaussianity,” Journal of Physics A: Mathematical and Theoretical 53, 075304 (2020).

Olivier Pinel, Julien Fade, Daniel Braun, Pu Jian, Nicolas Treps, and Claude Fabre, “Ultimate sensitivity of precision measurements with intense gaussian quantum light: A multimodal approach,” Phys. Rev. A 85, 010101 (2012).
Supplemental Material

I. MEAN FIELD SOLUTIONS

From the Hamiltonian in Eq. [1], the Heisenberg equations of motion are

\[
\frac{i\hbar}{\partial t} \hat{\psi}_a (r, t) = \left\{ -\frac{\hbar^2}{2m_a} \nabla^2 + V_a (r, t) + g_a \hat{\psi}_a (r, t) \hat{\psi}_a (r, t) + g_{am} \hat{\psi}_m (r, t) \hat{\psi}_m (r, t) \right\} \hat{\psi}_a (r, t) + \alpha \sqrt{2} \hat{\psi}_a (r, t) \hat{\psi}_m (r, t),
\]

\[
\frac{i\hbar}{\partial t} \hat{\psi}_m (r, t) = \left\{ -\frac{\hbar^2}{2m_m} \nabla^2 + V_m (r, t) + \epsilon + g_m \hat{\psi}_m (r, t) \hat{\psi}_m (r, t) + g_{am} \hat{\psi}_a (r, t) \hat{\psi}_a (r, t) \right\} \hat{\psi}_m (r, t) + \alpha \sqrt{2} \left( \hat{\psi}_a (r, t) \right)^2 .
\]

(S1)

By writing \( \hat{\psi}_a (r, t) = \hat{\psi}_{a,0} (r, t) e^{-i\int_0^t dt_1 V_a(r,t_1)/\hbar e^{-i\mu t/\hbar}} \) and \( \hat{\psi}_m (r, t) = \hat{\psi}_{m,0} (r, t) e^{-i\int_0^t dt_1 V_m(r,t_1)/\hbar e^{-2i\mu t/\hbar}} \), Eq. [S1] can be expressed as

\[
\frac{i\hbar}{\partial t} \hat{\psi}_{a,0} (r, t) = \left\{ -\frac{\hbar^2}{2m_a} \nabla^2 - \mu + g_a \hat{\psi}_{a,0} (r, t) \hat{\psi}_{a,0} (r, t) + g_{am} \hat{\psi}_{m,0} (r, t) \hat{\psi}_{m,0} (r, t) \right\} \hat{\psi}_{a,0} (r, t) + \alpha \sqrt{2} \hat{\psi}_{a,0} (r, t) \hat{\psi}_{m,0} (r, t) e^{-i\int_0^t dt_1 \left[ V_a(r,t_1) - 2V_m(r,t_1) \right]/\hbar}
\]

\[
+ \frac{\hbar^2}{2m_a} \left\{ \frac{1}{\hbar} \int_0^t dt_1 \nabla V_a (r, t_1) \right\}^2 + \frac{i}{\hbar} \int_0^t dt_1 \left[ \nabla^2 V_a (r, t_1) + 2 \left\{ \nabla V_a (r, t_1) \right\} \cdot \nabla \right] \hat{\psi}_{a,0} (r, t),
\]

\[
\frac{i\hbar}{\partial t} \hat{\psi}_{m,0} (r, t) = \left\{ -\frac{\hbar^2}{2m_m} \nabla^2 - \epsilon + \mu + g_m \hat{\psi}_{m,0} (r, t) \hat{\psi}_{m,0} (r, t) + g_{am} \hat{\psi}_{a,0} (r, t) \hat{\psi}_{a,0} (r, t) \right\} \hat{\psi}_{m,0} (r, t) + \frac{\alpha}{\sqrt{2}} \left( \hat{\psi}_{a,0} (r, t) \right)^2 e^{i\int_0^t dt_1 \left[ V_m(r,t_1) - 2V_m(r,t_1) \right]/\hbar}
\]

\[
+ \frac{\hbar^2}{2m_m} \left\{ \frac{1}{\hbar} \int_0^t dt_1 \nabla V_m (r, t_1) \right\}^2 + \frac{i}{\hbar} \int_0^t dt_1 \left[ \nabla^2 V_m (r, t_1) + 2 \left\{ \nabla V_m (r, t_1) \right\} \cdot \nabla \right] \hat{\psi}_{m,0} (r, t) .
\]

(S2)

Note that, according to Eqs. [S2], changing \( V_j (r, t) \) from 0 to \( V_j (t) \) \((j = a, m)\) does not affect \( \hat{\psi}_{j,0} (r, t) \) if \( V_m (t) = 2V_a (t) \).

By following [S1], in the Heisenberg picture, we split \( \hat{\psi}_j (r, t) \) as \( \hat{\psi}_j (r, t) = \hat{\psi}_j (r, t) \hat{\Phi}_{j,c} (t) + \delta \hat{\psi}_j (r, t) \) where \( \int d^3r \psi_j^* (r, t) \delta \psi_j (r, t) = 0 \). Then \( \hat{\Phi}_{j,c} (t) = \int d^3r \psi_j^* (r, t) \hat{\psi}_j (r, t) / \int d^3r |\psi_j (r, t)|^2 \) and from this result, one can get \( \hat{\Phi}_{j,c} (t) , \hat{\Phi}_{j,c}^+ (t) = 1/\int d^3r |\psi_j (r, t)|^2 \), \( \hat{\Phi}_{j,c} (t) , \delta \hat{\psi}_j (r, t) = \hat{\Phi}_{j,c} (t) , \delta \hat{\psi}_j (r, t) = 0 \), \( \delta \hat{\psi}_j (r, t) , \delta \hat{\psi}_j^+ (r', t) = \delta (r - r') \psi_j (r, t) \psi_j^+ (r', t) / \int d^3r |\psi_j (r, t)|^2 \), and \( \hat{\Phi}_{j,c}^+ (t) \hat{\Phi}_{j,c} (t) = N_{j,c} (t) / \int d^3r |\psi_j (r, t)|^2 \) where \( N_{a,c} (t) \) is the number of BEC atoms at time \( t \) and \( N_{m,c} (t) \) is the number of BEC molecules at time \( t \). From now on, we will set \( \int d^3r |\psi_j (r, t)|^2 = N_{j,c} (t) \) so that \( \psi_j (r, t) \) is the mean-field value of \( \hat{\psi}_j (r, t) \). Then we have \( \hat{\Phi}_{j,c}^+ (t) \hat{\Phi}_{j,c} (t) = 1 \) and for \( N_{j,c} (t) \gg 1 \), \( \hat{\Phi}_{j,c} (t) , \hat{\Phi}_{j,c}^+ (t) = 1/\sqrt{N_{j,c} (t)} \to 0 \). We will additionally substitute \( \hat{\Phi}_{j,c} (t) \to 1 \) for calculational convenience, which gives the usual non-number conserving approach \( \hat{\psi}_j (r, t) = \psi_j (r, t) + \delta \hat{\psi}_j (r, t) \).

Let \( N \) be the total number of BEC atoms (including the ones bound in molecules), \( V \) the volume of the system, and \( n := N/V \) the mean total number density of BEC atoms. For \( x (r, t) := |\psi_a (r, t)| / \sqrt{n} \) and \( y (r, t) := |\psi_m (r, t)| / \sqrt{n} \), we set

\[
\psi_a (r, t) = x (r, t) \sqrt{e^{-i\int_0^t dt_1 V_a(r,t_1)/\hbar e^{i(\varphi_a(r,t_1)-\mu t)/\hbar}}} , \quad \psi_m (r, t) = y (r, t) \sqrt{e^{-i\int_0^t dt_1 V_m(r,t_1)/\hbar e^{i(\varphi_m(r,t)-2\mu t)/\hbar}}} ,
\]

(S3)

which satisfy (note that \( m_m \simeq 2m_a \))
\[
\begin{align*}
\frac{i}{\hbar} \frac{\partial \varphi_a (r, t)}{\partial t} &= \left\{ \frac{\partial \varphi_a (r, t)}{\partial t} + \gamma_y y^2 (r, t) - \mu \right\} x (r, t) + \bar{\alpha} x (r, t) y (r, t) e^{i \varphi_m (r, t)} e^{-i \int^t dt_1 \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} / \hbar} \\
-\xi_a^2 \left\{ \nabla^2 x (r, t) - x (r, t) \left\{ \nabla \varphi_a (r, t) \right\}^2 + \frac{i}{x (r, t)} \nabla \cdot \left\{ x^2 (r, t) \left\{ \nabla \varphi_a (r, t) \right\} \right\} \right\} \\
+\xi_a \left\{ \left\{ x (r, t) \right\} + \frac{1}{\hbar} \int^t dt_1 \nabla V_m (r, t_1) \right\} x (r, t) \\
-2x^2 \left\{ \nabla \varphi_a (r, t) \right\} \cdot \left\{ \frac{1}{\hbar} \int^t dt_1 \nabla V_m (r, t_1) \right\} x (r, t), \\
\frac{i}{\hbar} \frac{\partial \varphi_m (r, t)}{\partial t} &= \left\{ \frac{\partial \varphi_m (r, t)}{\partial t} + \gamma_y y^2 (r, t) + \gamma_m x^2 (r, t) + \bar{\epsilon} - 2 \mu \right\} y (r, t) + \frac{\bar{\alpha}}{2} x^2 (r, t) e^{-i \varphi_m (r, t)} e^{i \int^t dt_1 \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} / \hbar} \\
-\xi_m^2 \left\{ \nabla^2 y (r, t) - y (r, t) \left\{ \nabla \varphi_m (r, t) \right\}^2 + \frac{i}{y (r, t)} \nabla \cdot \left\{ y^2 (r, t) \left\{ \nabla \varphi_m (r, t) \right\} \right\} \right\} \\
+\xi_m \left\{ \left\{ y (r, t) \right\} + \frac{1}{\hbar} \int^t dt_1 \nabla V_m (r, t_1) \right\} y (r, t) \\
-2y^2 \left\{ \nabla \varphi_m (r, t) \right\} \cdot \left\{ \frac{1}{\hbar} \int^t dt_1 \nabla V_m (r, t_1) \right\} y (r, t), \\
\end{align*}
\]

which give

\[
\begin{align*}
\int d^3 r \ x (r, t) \frac{\partial x (r, t)}{\partial t} &= \tilde{\alpha} \int d^3 r \ x^2 (r, t) y (r, t) \sin \left[ \varphi_m (r, t) - \frac{1}{\hbar} \int^t dt_1 \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} \right], \\
\int d^3 r \ y (r, t) \frac{\partial y (r, t)}{\partial t} &= -\frac{\tilde{\alpha}}{2} \int d^3 r \ x^2 (r, t) y (r, t) \sin \left[ \varphi_m (r, t) - \frac{1}{\hbar} \int^t dt_1 \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} \right],
\end{align*}
\]

and

\[
\frac{\partial \varphi_m (r, t)}{\partial t} = \xi_m^2 \left\{ \nabla^2 y (r, t) - \frac{\nabla \varphi_m (r, t)}{y (r, t)} \right\}^2 - 4y^2 + 4 \left\{ \nabla \varphi_a (r, t) \right\}^2 \\
-\frac{\xi_m^2}{2} \left\{ \frac{1}{\hbar} \int^t dt_1 \nabla \left\{ V_m (r, t_1) + 2 V_a (r, t_1) \right\} \right\} \cdot \left\{ \frac{1}{\hbar} \int^t dt_1 \nabla \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} \right\} \\
+\xi_m \left\{ \left\{ y (r, t) \right\} + \frac{1}{\hbar} \int^t dt_1 \nabla \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} \right\} + 2 \left\{ \nabla \varphi_m (r, t) \right\} \cdot \left\{ \frac{1}{\hbar} \int^t dt_1 \nabla V_m (r, t_1) \right\} \\
+2y^2 (r, t) + \gamma_m \left\{ 2y^2 (r, t) - x^2 (r, t) \right\} - \gamma_m y^2 (r, t) - \tilde{\epsilon} \\
+\frac{\tilde{\alpha}}{2} \left\{ 4y (r, t) - \frac{x^2 (r, t)}{y (r, t)} \right\} \cos \left[ \varphi_m (r, t) - \frac{1}{\hbar} \int^t dt_1 \left\{ V_m (r, t_1) - 2 V_a (r, t_1) \right\} \right].
\]

We normalize to atomic condensate units as follows: \( \tilde{\epsilon} := \sqrt{g_a n} / \hbar \), \( \bar{\alpha} := g_a / \sqrt{2 m_a g_a} \), \( \bar{\epsilon} := \epsilon / (g_a n) \), \( \xi_a := h / \sqrt{2 m_a g_a} \) is the atomic healing length, and \( \varphi_m (r, t) : = \varphi_m (r, t) - 2 \varphi_a (r, t) \).

When the system is in box traps \( V_a (r, t) = V_m (r, t) = 0 \) or \( V_m (r, t) = 2 V_a (r, t) = F_{1r} (t) \) where \( F_{1r} (t) \) is some real function which is homogeneous in space, Eqs. (S5) and (S6) can have solutions where \( x (r, t) \), \( y (r, t) \), and \( \varphi_m (r, t) \) do not depend on space.

This leads to the following conclusion: Suppose we add a spatially homogeneous density perturbation at \( t \geq 0 \) to the system with atoms and molecules trapped in box potentials. Let \( \psi_{j,0} (t) \) be the homogeneous mean-field of this system for \( t < 0 \) and \( \psi_{j,1} (r, t) \) be the mean-field of the system for \( t \geq 0 \) \((j = a, m) \). Then, from Eqs. (S5) and (S6), \( \psi_{j,1} (r, t) = \psi_{j,0} (t) e^{-i \int^t_0 dt_1 V_j (t_1) / \hbar} \). From now on, we will consider these homogeneous solutions whose mean-field Hamiltonian \( H_0 (t) \) is

\[
H_0 (t) / (N g_a n) = \frac{1}{2} x^4 \left( t \right) + \frac{\gamma_m}{2} y^4 \left( t \right) + \tilde{\epsilon} y^2 \left( t \right) + \gamma_m x^2 \left( t \right) y^2 \left( t \right) + \bar{\alpha} x^2 \left( t \right) y \left( t \right) \cos \varphi_m \left( t \right)
+ V_a \left( t \right) x^2 \left( t \right) + V_m \left( t \right) y^2 \left( t \right) / g_an, \quad (S7)
\]
Thus, by assuming \( g_\alpha > 0 \), \( H_0(t) \) is minimized when \( \alpha \cos \varphi_{am}(t) = -|\alpha| \). Since \( \alpha \cos \varphi_{am}(t) = -|\alpha| \) makes \( \sin \varphi_{am} = 0 \), which forces \( x(t) \) and \( y(t) \) to be constant according to Eqs. (S5), from now on, we will write \( x(t) \) as \( x \) and \( y(t) \) as \( y \).

From Eq. (S6), \( \alpha \cos \varphi_{am}(t) = -|\alpha| \) can be achieved when

\[
\bar{e} = 2x^2 + \bar{g}_{am}(2y^2 - x^2) - \frac{|\alpha|}{2} \left( 4y - \frac{x^2}{y} \right). \tag{S8}
\]

Using Eqs. (S7) and (S8), one can get

\[
\frac{H_0}{Ng_{\alpha n}} = \frac{V_a(t) x^2 + V_m(t) y^2}{g_{\alpha n}} + \frac{1}{2}x^4 - \frac{1}{2} (\bar{g}_{m} - 4\bar{g}_{am}) y^4 + 2x^2y^2 - 2|\alpha| y^3 - \frac{|\alpha|}{2} x^2 y, \tag{S9}
\]

where \( x^2 + 2y^2 = 1 \) from number conservation in Eq. (2).

Now, let \( \varphi_x(t) \) and \( \varphi_m(t) \) to be also constant in time \( t \). From Eq. (S4), these conditions can be achieved when

\[
\bar{\mu} = x^2 + \bar{g}_{am} y^2 - |\alpha| y. \tag{S10}
\]

With Eqs. (2), (S9), and (S10),

\[
\frac{H_0 - \mu N}{Ng_{\alpha n}} = -\frac{1}{2} - \left\{ 2 + \frac{1}{2} (\bar{g}_{m} - 4\bar{g}_{am}) \right\} y^4 + (2 - \bar{g}_{am}) y^3 + \frac{|\alpha|}{2} y + \frac{V_a(t) + \{V_m(t) - 2V_a(t)\}}{g_{\alpha n}} y^2. \tag{S11}
\]

For the case of the box traps or \( V_m(t) = 2V_a(t) \), the energy in Eq. (S11) is minimized when

\[
(8 + 2\bar{g}_m - 8\bar{g}_{am}) y^3 + 3|\alpha| y^2 - 2 (2 - \bar{g}_{am}) y - \frac{|\alpha|}{2} = 0, \tag{S12}
\]

with \( y \geq 0 \) and \( x = \sqrt{1 - 2y^2} \) from number conservation.

II. BOGOLIUBOV EXPANSION

In the Heisenberg picture, by writing \( \hat{\psi}_j(r,t) = \psi_j(r,t) + \delta \hat{\psi}_j(r,t) \) with

\[
\delta \hat{\psi}_a(r,t) = e^{-i\int t d_t V_a(r,t)/\hbar} e^{-i\mu t/\hbar} \frac{1}{\sqrt{V}} \sum_{k \neq 0} e^{ikr} \delta \hat{\Psi}_a(k,t),
\]

\[
\delta \hat{\psi}_m(r,t) = e^{-i\int t d_t V_m(r,t)/\hbar} e^{-i2\mu t/\hbar} \frac{1}{\sqrt{V}} \sum_{k \neq 0} e^{ikr} \delta \hat{\Psi}_m(k,t), \tag{S13}
\]

from the commutation relations \( \left[ \hat{\psi}_j(r_1,t), \hat{\psi}_l^\dagger(r_2,t) \right] = \delta_{j,l} \delta (r_1 - r_2) \) and \( \left[ \hat{\psi}_j(r_1,t), \hat{\psi}_l(t_2,r_2) \right] = 0 \) for \( j = a, m \) and \( l = a, m \), one can get

\[
\left[ \delta \hat{\Psi}_j(k_1,t), \delta \hat{\Psi}_l^\dagger(k_2,t) \right] = \delta_{j,l} \delta_{k_1,k_2}, \quad \left[ \delta \hat{\Psi}_j(k_1,t), \delta \hat{\Psi}_l(k_2,t) \right] = 0. \tag{S14}
\]

For box trap case \( V_a(r,t) = 0 \) and \( V_m(r,t) = 0 \) or \( V_m(t) = 2V_a(t) \), with solutions \( \psi_a(r,t) = x\sqrt{n} e^{-i\int t d_t V_a(r,t)/\hbar} e^{i(\varphi_a - \mu t/\hbar)} \) and \( \psi_m(r,t) = y\sqrt{n} e^{-i\int t d_t V_m(r,t)/\hbar} e^{i(\varphi_m - 2\mu t/\hbar)} \) where \( x, y, \varphi_a, \) and \( \varphi_m \) are constant in time \( t \) by satisfying Eq. (S10) and \( \alpha \cos \varphi_{am}(t) = -|\alpha| \) by satisfying Eq. (S8), up to second order in \( \delta \hat{\Psi}_j \) where \( j = a, m \), \( \hat{H}(t) - \mu \hat{N} \) can be written as

\[
\hat{H}(t) - \mu \hat{N} = H_0 - \mu N - \frac{g_{\alpha n}}{2} \sum_{k \neq 0} \left\{ M_{11}(k) + M_{22}(k) \right\} + O \left( \delta \hat{\Psi}_j^3 \right)
\]

\[
+ \frac{g_{\alpha n}}{2} \sum_{k \neq 0} \left[ \delta \hat{\Psi}_a^\dagger(k,t) \delta \hat{\Psi}_m(k,t) \delta \hat{\Psi}_a(-k,t) \delta \hat{\Psi}_m(-k,t) \right] \left[ \begin{array}{cccc} M_{11}(k) & M_{12} & M_{13} & M_{14} \\
M_{12} & M_{22}(k) & M_{14} & M_{24} \\
M_{13} & M_{14} & M_{11}(k) & M_{12} \\
M_{14} & M_{24} & M_{12} & M_{22}(k) \end{array} \right] \left[ \begin{array}{cc}
\delta \hat{\Psi}_a(k,t) \\
\delta \hat{\Psi}_m(k,t) \\
\delta \hat{\Psi}_a(-k,t) \\
\delta \hat{\Psi}_m(-k,t) \end{array} \right]
\]

\[
+ V_a(t) \sum_{k \neq 0} \left\{ \delta \hat{\Psi}_a^\dagger(k,t) \delta \hat{\Psi}_a(k,t) + 2 \delta \hat{\Psi}_m^\dagger(k,t) \delta \hat{\Psi}_m(k,t) \right\}, \tag{S15}
\]
where \( \mu \) is in Eq. (S10), \( H_0 - \mu N \) in Eq. (S11).

\[
M_{11} (k) := \frac{\hbar^2 k^2}{2m a_n} + 2x^2 + \tilde{g}_a y^2 - \tilde{\mu} = k^2 x_a^2 + 1 - 2y^2 + |\alpha| y,
\]

(S16)

\[
M_{22} (k) := \frac{\hbar^2 k^2}{2m a_n} + \tilde{\epsilon} + 2\tilde{g}_a y^2 + \tilde{\tilde{g}} y^2 - 2\tilde{\mu} = \frac{1}{2} k^2 \xi_a^2 + \tilde{g}_a y^2 - |\alpha| \left( y - \frac{1}{2y} \right),
\]

(S17)

\[
M_{12} := \{ \alpha - \text{sign}(\alpha) \tilde{g}_a y \} \sqrt{1 - 2y^2}, \quad M_{13} := 1 - 2y^2 - |\alpha| y, \quad M_{14} := -\text{sign}(\alpha) \tilde{g}_a y \sqrt{1 - 2y^2}, \quad M_{24} := \tilde{g}_a y^2.
\]

(S18)

Here, for convenience, we set \( \varphi_a = 0 \) and define \( \text{sign}(\alpha) = 1 \) if \( \alpha \geq 0 \) and \( \text{sign}(\alpha) = -1 \) if \( \alpha < 0 \).

We define the \( 4 \times 4 \) matrix \( M (k) \) as

\[
M (k) := \begin{bmatrix}
M_{11} (k) & M_{12} & M_{13} & M_{14} \\
M_{12}^* & M_{22} (k) & M_{14} & M_{24} \\
M_{13} & M_{14} & M_{11} (k) & M_{12}^* \\
M_{14} & M_{24} & M_{12} & M_{22} (k)
\end{bmatrix} = \begin{bmatrix}
M_{B,1} (k) & M_{B,2} \\
M_{B,2}^* & M_{B,1} (k)
\end{bmatrix},
\]

(S19)

with \( 2 \times 2 \) matrices \( M_{B,1,2} \) (\( \zeta = 1, 2 \)).

According to Eq. (S15), a system with \( V_m (t) = 2V_a (t) \neq 0 \) can be interpreted as a system in a box trap with an additional perturbation \( \tilde{V}_H (t) = V_a (t) \int d^3r \left\{ \psi_0^\dagger (r, t) \psi_0 (r, t) + 2\psi_0^\dagger (r, t) \tilde{\psi}_m (r, t) \right\} \). In the following we first focus on the case \( \tilde{V}_H = 0 \), and consider perturbations later in section IV. Then, from Bogoliubov expansion [37, 52], we may write

\[
\begin{bmatrix}
\delta \hat{\Psi}_a (k, t) \\
\delta \hat{\Psi}_m (k, t) \\
\delta \hat{\Psi}_m^\dagger (k, t) \\
\delta \hat{\Psi}_m^\dagger (k, t)
\end{bmatrix} = \begin{bmatrix}
U (k) & V^* (k) \\
V (k) & U^* (k)
\end{bmatrix} \begin{bmatrix}
\hat{b}_1 (k, t) \\
\hat{b}_2 (k, t)
\end{bmatrix},
\]

(S20)

where \( U (k) \) and \( V (k) \) are \( 2 \times 2 \) matrices and \( \hat{b}_p (k, t) \) are bosonic annihilation operators \( (p = 1, 2) \).

If \( \left[ \hat{b}_p (k_1, t), \hat{b}_q^\dagger (k_2, t) \right] = \delta_{p,q} \delta_{k_1, k_2} \) and \( \left[ \hat{b}_p (k_1, t), \hat{b}_q (k_2, t) \right] = 0 \) for \( p, q = 1, 2 \),

\[
\delta_{k_1, k_2} \{ U (k_1) U^\dagger (k_1) - V^* (k_1) V^T (k_1) \} = \delta_{k_1, k_2} I, \quad \delta_{k_1, -k_2} \{ U (k_1) V^\dagger (k_1) - V^* (k_1) U^T (k_1) \} = 0.
\]

(S21)

Thus, we will set

\[
U (k) U^\dagger (k) - V^* (k) V^T (k) := I, \quad U (k) V^\dagger (k) - V^* (k) U^T (k) := 0.
\]

(S22)

Then one can get

\[
U^\dagger (k) U (k) - V^\dagger (k) V (k) = I, \quad U^\dagger (k) V^* (k) - V^\dagger (k) U^* (k) = 0.
\]

(S23)

By following the approach in [37], suppose that \( M_{B,2} \), \( U (k) \), and \( V (k) \) satisfy

\[
g_{a_n} \begin{bmatrix}
M_{B,1} (k) & M_{B,2} \\
-M_{B,2}^* & -M_{B,1} (k)
\end{bmatrix} \begin{bmatrix}
U (k) \\
V (k)
\end{bmatrix} = \begin{bmatrix}
U (k) \\
V (k)
\end{bmatrix} \mathcal{E} (k), \quad \text{where} \ \mathcal{E} (k) := \hbar \begin{bmatrix}
\omega_1 (k) & 0 \\
0 & \omega_2 (k)
\end{bmatrix}.
\]

(S24)

Let \( \sigma_z := \begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix} \). Then, from Eq. (S24), \( \mathcal{V} (k) := \begin{bmatrix}
U (k) \\
V (k)
\end{bmatrix} \) is the \( 4 \times 2 \) eigenmatrix of \( \sigma_z M (k) \) and Eq. (S23) can be written as

\[
\mathcal{V}^\dagger (k) \begin{bmatrix}
I & 0 \\
0 & -I
\end{bmatrix} \mathcal{V} (k) = I.
\]

(S25)

Note that if Eq. (S24) is satisfied,

\[
g_{a_n} \begin{bmatrix}
M_{B,1} (k) & M_{B,2} \\
-M_{B,2}^* & -M_{B,1} (k)
\end{bmatrix} \begin{bmatrix}
V^* (k) \\
U^* (k)
\end{bmatrix} = -\begin{bmatrix}
V^* (k) \\
U^* (k)
\end{bmatrix} \mathcal{E}^* (k),
\]

(S26)
so \( \begin{bmatrix} V^\dagger (k) & U^\dagger (k) \end{bmatrix}^T \) is also eigenmatrix of \( \sigma_z M (k) \).

However,

\[
\begin{bmatrix} V^* (k) \\ U^* (k) \end{bmatrix}^T \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} V^* (k) \\ U^* (k) \end{bmatrix} = - \{ U^\dagger (k) U (k) - V^\dagger (k) V (k) \}^* = -I, \tag{S27}
\]

and thus it does not satisfy Eq. (S25). Therefore, half of the eigenvalues are unphysical values (in the sense that their eigenmatrices \( V (k) \) do not satisfy Eq. (S25) and hence bosonic commutation relations are not satisfied).

After discarding those unphysical eigenvalues, Eq. (S15) can be written as

\[
\hat{H} (t) - \mu \hat{N} = H_0 - \mu N + \frac{1}{2} \sum_{k \neq 0} \left[ \hbar \{ \omega_1 (k) + \omega_2 (k) \}^* - g_{a,n} \{ M_{11} (k) + M_{22} (k) \} \right]
\]

\[
+ \hbar \sum_{k \neq 0} \left[ \text{Re} \{ \omega_1 (k) \} \hat{b}_1^\dagger (k, t) \hat{b}_1 (k, t) + \text{Re} \{ \omega_2 (k) \} \hat{b}_2^\dagger (k, t) \hat{b}_2 (k, t) \right] + O \left( \delta \hat{\Psi}^3 \right). \tag{S28}
\]

From [37], by writing

\[
U (k) := \begin{bmatrix} u_1 (k) & u_2 (k) \end{bmatrix}, \quad V (k) := \begin{bmatrix} v_1 (k) & v_2 (k) \end{bmatrix}, \tag{S29}
\]

where \( u_p (k) = \begin{bmatrix} u_{p1} (k) & u_{p2} (k) \end{bmatrix}^T \) and \( v_p (k) = \begin{bmatrix} v_{p1} (k) & v_{p2} (k) \end{bmatrix}^T \) are \( 2 \times 1 \) matrices \((p = 1, 2)\), Eq. (S24) can be written as

\[
\begin{bmatrix} M_{B1,1} (k) & M_{B1,2} \\ -M_{B1,1}^* & -M_{B1,2}^* \end{bmatrix} \begin{bmatrix} u_p (k) \\ v_p (k) \end{bmatrix} = \tilde{\omega}_p (k) \begin{bmatrix} u_p (k) \\ v_p (k) \end{bmatrix}, \tag{S30}
\]

where \( \tilde{\omega}_p (k) := \hbar \omega_p (k) / (g_{a,n}) \). Note that, if \( M_{B1,1} (k) \), \( M_{B1,2} \), and \( \tilde{\omega}_p (k) \) are all real, then \( u_p (k) \) and \( v_p (k) \) should be also real from Eq. (S30).

In terms of the above eigenvectors, the \( 4 \times 4 \) eigenproblem reads

\[
\begin{bmatrix} M_{11} (k) & M_{12} & M_{13} & M_{14} \\ M_{21}^* & M_{22} & M_{23}^* & M_{24} \\ -M_{31}^* & -M_{32} & -M_{33}^* & -M_{34}^* \\ -M_{41}^* & -M_{42} & -M_{43}^* & -M_{44}^* \end{bmatrix} \begin{bmatrix} u_{p1} (k) \\ u_{p2} (k) \\ v_{p1} (k) \\ v_{p2} (k) \end{bmatrix} = \tilde{\omega}_p (k) \begin{bmatrix} u_{p1} (k) \\ u_{p2} (k) \\ v_{p1} (k) \\ v_{p2} (k) \end{bmatrix}, \tag{S31}
\]

where \( \zeta_{11} \) is defined from Eqs. (S16) to (S18) \((\zeta, \eta = 1, 2)\).

Now, to get \( \tilde{\omega}_p (k) \) and its eigenvector \( \begin{bmatrix} u_{p1} (k) & u_{p2} (k) & v_{p1} (k) & v_{p2} (k) \end{bmatrix}^T \), we will follow [36] and introduce

\[
\begin{bmatrix} \delta \hat{\Psi}_a (k, t) \\ \delta \hat{\Psi}_m (k, t) \\ \delta \hat{\Psi}_d^\dagger (-k, t) \\ \delta \hat{\Psi}_d^\dagger (k, t) \end{bmatrix} = \begin{bmatrix} \cos \phi (k) & -\sin \phi (k) & 0 & 0 \\ \sin \phi (k) & \cos \phi (k) & 0 & 0 \\ 0 & 0 & \cos \phi (k) & -\sin \phi (k) \\ 0 & 0 & \sin \phi (k) & \cos \phi (k) \end{bmatrix} \begin{bmatrix} \delta \hat{\Psi}_{R,1} (k, t) \\ \delta \hat{\Psi}_{R,2} (k, t) \\ \delta \hat{\Psi}_{R,1} (-k, t) \\ \delta \hat{\Psi}_{R,2} (-k, t) \end{bmatrix}, \tag{S32}
\]

and define \( \Theta (k) := \begin{bmatrix} \cos \phi (k) & -\sin \phi (k) \\ \sin \phi (k) & \cos \phi (k) \end{bmatrix} \). Note that \( \Theta (k) \) is real \( 2 \times 2 \) matrix and \( \Theta^{-1} (k) = \Theta^T (k) \). It is trivial to check that \( \delta \hat{\Psi}_{R,1} (k, t) \) and \( \delta \hat{\Psi}_{R,2} (k, t) \) are independent bosonic operators.

From the second line in Eq. (S15), \( M (k) \) is transformed to

\[
\begin{bmatrix} \Theta (k) & 0 \\ 0 & \Theta (k) \end{bmatrix}^{-1} M (k) \begin{bmatrix} \Theta (k) & 0 \\ 0 & \Theta (k) \end{bmatrix} = \begin{bmatrix} A_{11} (k) & A_{12} (k) & A_{13} (k) & A_{14} (k) \\ A_{12} (k) & A_{22} (k) & A_{23} (k) & A_{24} (k) \\ A_{13} (k) & A_{23} (k) & A_{33} (k) & A_{34} (k) \\ A_{14} (k) & A_{24} (k) & A_{34} (k) & A_{44} (k) \end{bmatrix}, \tag{S33}
\]

where

\[
A_{13} (k) := M_{13} \cos^2 \phi (k) + M_{24} \sin^2 \phi (k) + M_{14} \sin \{ 2 \phi (k) \},
\]

\[
= 1 - 2y^2 - |\bar{\alpha}| y + \bar{g}_m y^2 + \frac{1}{2} - 2y^2 - |\bar{\alpha}| y - \bar{g}_m y^2 \cos \{ 2 \phi (k) \} - \text{sign} (\alpha) \bar{g}_{am} y \sqrt{1 - 2y^2} \sin \{ 2 \phi (k) \}. \tag{S34}
\]
\[
A_{14} (k) := M_{14} \cos \{2 \phi (k)\} - \frac{1}{2} (M_{13} - M_{24}) \sin \{2 \phi (k)\},
\]
\[
= - \text{sign} (\alpha) \bar{g}_m y \sqrt{1 - 2y^2} \cos \{2 \phi (k)\} - \frac{1}{2} (1 - 2y^2 - |\alpha| y - \bar{g}_m y^2) \sin \{2 \phi (k)\},
\]  
(S35)

\[
A_{24} (k) := M_{24} \cos^2 \phi (k) + M_{13} \sin^2 \phi (k) - M_{14} \sin \{2 \phi (k)\},
\]
\[
= \frac{1 - 2y^2 - |\alpha| y + \bar{g}_m y^2}{2} - \frac{1 - 2y^2 - |\alpha| y - \bar{g}_m y^2}{2} \cos \{2 \phi (k)\} + \text{sign} (\alpha) \bar{g}_m y \sqrt{1 - 2y^2} \sin \{2 \phi (k)\},
\]  
(S36)

\[
A_{11} (k) := M_{11} \cos^2 \phi (k) + M_{22} \sin^2 \phi (k) + \text{Re} (M_{12}) \sin \{2 \phi (k)\}
\]
\[
= \tilde{\omega}_c (k) \cos^2 \phi (k) + \tilde{\omega}_d (k) \sin^2 \phi (k) + \tilde{\alpha} \sqrt{1 - 2y^2} \sin \{2 \phi (k)\} + A_{13} (k),
\]  
(S37)

\[
A_{22} (k) := M_{22} \cos^2 \phi (k) + M_{11} \sin^2 \phi (k) - \text{Re} (M_{12}) \sin \{2 \phi (k)\},
\]
\[
= \tilde{\omega}_d (k) \cos^2 \phi (k) + \tilde{\omega}_c (k) \sin^2 \phi (k) - \tilde{\alpha} \sqrt{1 - 2y^2} \sin \{2 \phi (k)\} + A_{24} (k),
\]  
(S38)

\[
A_{12} (k) := M_{12} \cos^2 \phi (k) - M_{12}^* \sin^2 \phi (k) - \frac{1}{2} \{M_{11} (k) - M_{22} (k)\} \sin \{2 \phi (k)\},
\]
\[
= \tilde{\alpha} \sqrt{1 - 2y^2} \cos \{2 \phi (k)\} - \frac{1}{2} \{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\} \sin \{2 \phi (k)\} + A_{14} (k),
\]  
(S39)

\[
\tilde{\omega}_a (k) := k^2 \xi_d^2 + 2 |\alpha| y, \text{ and } \tilde{\omega}_d (k) := (k^2 \xi_d^2 / 2) + |\alpha| (1 - 2y^2) / (2y).
\]

Now, let \( \tilde{\omega}_{a1} (k) := \tilde{\omega}_c (k) \cos^2 \phi (k) + \tilde{\omega}_d (k) \sin^2 \phi (k) + \tilde{\alpha} \sqrt{1 - 2y^2} \sin \{2 \phi (k)\} \), and \( \tilde{\omega}_{a2} (k) := \tilde{\omega}_c (k) \sin^2 \phi (k) + \tilde{\omega}_d (k) \cos^2 \phi (k) - \tilde{\alpha} \sqrt{1 - 2y^2} \sin \{2 \phi (k)\} \). By setting \( \{2 \phi (k)\} = 2 \tilde{\alpha} \sqrt{1 - 2y^2} / \{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\} \) so that \( A_{12} (k) = A_{14} (k) \), the Bogoliubov 4 \times 4 eigenproblem becomes

\[
\begin{pmatrix}
\tilde{\omega}_{a1} (k) + A_{13} (k) & A_{14} (k) \\
A_{14} (k) & \tilde{\omega}_{a2} (k) + A_{24} (k) \\
-A_{13} (k) & A_{14} (k) \\
-A_{14} (k) & -A_{24} (k)
\end{pmatrix}
\begin{pmatrix}
A_{13} (k) \\
A_{14} (k) \\
-A_{13} (k) \\
-A_{14} (k)
\end{pmatrix}
\begin{pmatrix}
A_{13} (k) \\
A_{14} (k) \\
-A_{13} (k) \\
-A_{14} (k)
\end{pmatrix}
\begin{pmatrix}
A_{14} (k) \\
A_{24} (k) \\
-A_{14} (k) \\
-A_{24} (k)
\end{pmatrix}
= \begin{pmatrix}
\tilde{u}_{R,p1} (k) \\
\tilde{u}_{R,p2} (k) \\
\tilde{v}_{R,p1} (k) \\
\tilde{v}_{R,p2} (k)
\end{pmatrix},
\]  
(S40)

where

\[
\tilde{\omega}_{a1} (k) = \frac{\tilde{\omega}_c (k) + \tilde{\omega}_d (k) + \sqrt{\{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\}^2 + 4 \tilde{\alpha}^2 (1 - 2y^2)}}{2},
\]  
(S41)

\[
\tilde{\omega}_{a2} (k) = \frac{\tilde{\omega}_c (k) + \tilde{\omega}_d (k) - \sqrt{\{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\}^2 + 4 \tilde{\alpha}^2 (1 - 2y^2)}}{2},
\]  
(S42)

\[
A_{13} (k) = \frac{1 - 2y^2 - |\alpha| y + \bar{g}_m y^2}{2} + \frac{(1 - 2y^2 - |\alpha| y - \bar{g}_m y^2) \{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\} - 4 |\alpha| \bar{g}_m y (1 - 2y^2)}{2 \sqrt{\{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\}^2 + 4 \tilde{\alpha}^2 (1 - 2y^2)}},
\]  
(S43)

\[
A_{14} (k) = - \text{sign} (\alpha) \sqrt{1 - 2y^2} \bar{g}_m y \{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\} + \tilde{\alpha} (1 - 2y^2 - |\alpha| y - \bar{g}_m y^2) \sqrt{\{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\}^2 + 4 \tilde{\alpha}^2 (1 - 2y^2)},
\]  
(S44)

\[
A_{24} (k) = \frac{1 - 2y^2 - |\alpha| y + \bar{g}_m y^2}{2} - \frac{(1 - 2y^2 - |\alpha| y - \bar{g}_m y^2) \{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\} - 4 |\alpha| \bar{g}_m y (1 - 2y^2)}{2 \sqrt{\{\tilde{\omega}_c (k) - \tilde{\omega}_d (k)\}^2 + 4 \tilde{\alpha}^2 (1 - 2y^2)}},
\]  
(S45)

\[U (k) = \Theta (k) U_R (k), \text{ and } V (k) = \Theta (k) V_R (k)\] with
\[
U_R(k) := \begin{bmatrix} u_{R,11}(k) & u_{R,21}(k) \\ u_{R,12}(k) & u_{R,22}(k) \end{bmatrix}, \quad V_R(k) := \begin{bmatrix} v_{R,11}(k) & v_{R,21}(k) \\ v_{R,12}(k) & v_{R,22}(k) \end{bmatrix}.
\] (S46)

Since \( \Theta^{-1}(k) = \Theta^T(k) = \Theta^i(k) \), \( U_R(k) \) and \( V_R(k) \) satisfy Bogoliubov conditions in Eqs. (S22) and (S23). Then one can get

\[
\tilde{\omega}_p(k) = \sqrt{\frac{\tilde{\omega}_{a1}^2(k) + \tilde{\omega}_{a2}^2(k) + (2p-3)\sqrt{\left(\tilde{\omega}_{a1}^2(k) - \tilde{\omega}_{a2}^2(k)\right)^2 + 16A_{14}^2(k)\tilde{\omega}_{a1}(k)\tilde{\omega}_{a2}(k)}}{2}},
\] (S47)

which is same as \( \text{(30)} \) where \( \tilde{\omega}_{a1}^2(k) := \tilde{\omega}_{a1}(k)\{\tilde{\omega}_{a1}(k) + 2A_{13}(k)\} \) and \( \tilde{\omega}_{a2}^2(k) := \tilde{\omega}_{a2}(k)\{\tilde{\omega}_{a2}(k) + 2A_{24}(k)\} \). Note that \( \tilde{\omega}_p(k) \) is independent of the sign of \( \tilde{\alpha} \), since \( \tilde{\omega}_{a1}^2(k), \tilde{\omega}_{a2}^2(k), \) and \( A_{14}^2(k) \) depend on \( |\tilde{\alpha}| \).

From Eq. (S47), as long as \( 0 \leq y \leq 1/\sqrt{2} \) (physical values of \( y \)), \( \tilde{\omega}_2(k) \) is always real and \( \tilde{\omega}_1(k) \) is real if \( \{\tilde{\omega}_{a1}(k) + 2A_{13}(k)\} \{\tilde{\omega}_{a2}(k) + 2A_{24}(k)\} \geq 4A_{14}^2(k) \).

Expanding in terms of \( k^2 \), one can get

\[
\tilde{\omega}_{a1}(k) = \frac{|\tilde{\alpha}|(1 + 2y^2)}{2y} + \frac{6y^2 + 1}{2(1 + 2y^2)}k^2\xi_a^2 + O(k^4), \quad \tilde{\omega}_{a2}(k) = -\frac{1}{1 + 2y^2}k^2\xi_a^2 + O(k^4),
\] (S48)

\[
A_{13}(k) = \frac{y^2\left\{(4 - 4\tilde{g}_{am} - \tilde{g}_m) (1 - 2y^2) - 4|\tilde{\alpha}|y\right\}}{1 + 2y^2} - \frac{4y^3(1 - 2y^2)\left\{\tilde{g}_{am} - 2 - 2(3\tilde{g}_{am} - \tilde{g}_m - 2)y^2 + 2|\tilde{\alpha}|y\right\}k^2\xi_a^2}{|\tilde{\alpha}|(1 + 2y^2)^3} + O(k^4),
\] (S49)

\[
A_{24}(k) = \frac{1 + 4(\tilde{g}_{am} - 1)y^2 - 4(2\tilde{g}_{am} - 1 - \tilde{g}_m)y^4 - |\tilde{\alpha}|y (1 - 2y^2)}{1 + 2y^2} + \frac{4y^3(1 - 2y^2)\left\{\tilde{g}_{am} - 2 - 2(3\tilde{g}_{am} - \tilde{g}_m - 2)y^2 + 2|\tilde{\alpha}|y\right\}k^2\xi_a^2}{|\tilde{\alpha}|(1 + 2y^2)^3} + O(k^4),
\] (S50)

and

\[
A_{14}(k) = \text{sign}(\alpha)\frac{y\sqrt{1 - 2y^2}}{1 + 2y^2}\left\{\tilde{g}_{am} - 2 - 2(3\tilde{g}_{am} - \tilde{g}_m - 2)y^2 + 2|\tilde{\alpha}|y\right\}
\]

\[+ \frac{2\text{sign}(\alpha)\sqrt{1 - 2y^2}}{|\tilde{\alpha}|(1 + 2y^2)^3}\left\{|\tilde{\alpha}|y (1 - 6y^2) - 1 - (8\tilde{g}_{am} - \tilde{g}_m - 8)y^2 + 2(8\tilde{g}_{am} - 3\tilde{g}_m - 6)y^4\right\}k^2\xi_a^2 + O(k^4).
\] (S51)

Thus,

\[
\tilde{\omega}_{a1}^2(k) = |\tilde{\alpha}|\left(1 - 2y^2\right)\left\{|\tilde{\alpha}|\left(1 + 6y^2\right) - 4(4\tilde{g}_{am} - \tilde{g}_m - 4)y^3\right\}k^2\xi_a^2 + O(k^4),
\] (S52)

\[
\tilde{\omega}_{a2}^2(k) = 2\frac{1 + 4(\tilde{g}_{am} - 1)y^2 - 4(2\tilde{g}_{am} - \tilde{g}_m - 1)y^4 - |\tilde{\alpha}|y (1 - 2y^2)}{(1 + 2y^2)^2}k^2\xi_a^2 + O(k^4),
\] (S53)

and

\[
16A_{14}^2(k)\tilde{\omega}_{a1}(k)\tilde{\omega}_{a2}(k) = 8|\tilde{\alpha}|\frac{y(1 - 2y^2)}{(1 + 2y^2)^2}\left\{\tilde{g}_{am} - 2 - 2(3\tilde{g}_{am} - \tilde{g}_m - 2)y^2 + 2|\tilde{\alpha}|y\right\}k^2\xi_a^2 + O(k^4). \] (S54)

For notational convenience, by introducing

\[
A_1 := |\tilde{\alpha}|(1 - 2y^2)\frac{|\tilde{\alpha}|(1 + 6y^2) - 4(4\tilde{g}_{am} - \tilde{g}_m - 4)y^3}{4y^2},
\] (S55)
\[ B_1 := \frac{2y^3 (1 - 2y^2) \{ 12 - 8\tilde{g}_{am} + \tilde{g}_m - 2(\tilde{g}_m - 4) y^2 \} + |\tilde{\alpha}| \{ 8y^6 + 4y^4 + 10y^2 + 1 \}}{2y (1 + 2y^2)^2}, \]  
(S56)

\[ B_2 := \frac{2 \left( 1 + 4(\tilde{g}_{am} - 1) y^2 - 4(2\tilde{g}_{am} - \tilde{g}_m - 1) y^4 - |\tilde{\alpha}| y (1 - 2y^2) \right)}{(1 + 2y^2)^2}, \]  
(S57)

and

\[ B_3 := 8 |\tilde{\alpha}| \frac{y (1 - 2y^2)}{(1 + 2y^2)^2} \left\{ \tilde{g}_{am} - 2 - 2(3\tilde{g}_{am} - \tilde{g}_m - 2) y^2 + 2 |\tilde{\alpha}| y \right\}^2, \]  
(S58)

we get

\[ \tilde{\omega}_1 (k) = \sqrt{\frac{A_1 - |A_1|}{2} + k^2 \xi_a} \left( \frac{A_1 - |A_1|}{2A_1} B_1 + \frac{A_1 + |A_1|}{2A_1} B_2 - \frac{B_3}{4 |A_1|} \right) + O (k^4), \]

\[ \tilde{\omega}_2 (k) = \sqrt{\frac{A_1 + |A_1|}{2} + k^2 \xi_a} \left( \frac{A_1 + |A_1|}{2A_1} B_1 + \frac{A_1 - |A_1|}{2A_1} B_2 + \frac{B_3}{4 |A_1|} \right) + O (k^4). \]  
(S59)

If \( A_1 > 0 \),

\[ \tilde{\omega}_1 (k) = k \xi_a \sqrt{B_2 - \frac{B_3}{4 |A_1|}} + O (k^2), \quad \tilde{\omega}_2 (k) = \sqrt{A_1 + k^2 \xi_a} \left( B_1 + \frac{B_3}{4 |A_1|} \right) + O (k^4). \]  
(S60)

From Eq. (S40), one can get

\[ u_{R,p2} (k) = -\frac{\tilde{\omega}_2 (k) + \tilde{\omega}_p (k) \tilde{\omega}_a^2 (k) - \tilde{\omega}_p^2 (k)}{\tilde{\omega}_a (k) + \tilde{\omega}_p (k) 2\tilde{\omega}_a^2 (k) A_{14} (k)} u_{R,p1} (k), \quad v_{R,p1} (k) = \frac{\tilde{\omega}_a (k) - \tilde{\omega}_p (k)}{\tilde{\omega}_a (k) + \tilde{\omega}_p (k)} u_{R,p1} (k), \]

\[ v_{R,p2} (k) = -\frac{\tilde{\omega}_a (k) - \tilde{\omega}_p (k) \tilde{\omega}_a^2 (k) - \tilde{\omega}_p^2 (k)}{\tilde{\omega}_a (k) + \tilde{\omega}_p (k) 2\tilde{\omega}_a^2 (k) A_{14} (k)} u_{R,p1} (k). \]  
(S61)

From Eqs. (S22) and (S23),

\[ |u_{R,11} (k)|^2 + |u_{R,21} (k)|^2 - |v_{R,11} (k)|^2 = 1, \]  
(S62)

\[ |u_{R,12} (k)|^2 + |u_{R,22} (k)|^2 - |v_{R,22} (k)|^2 = 1, \]  
(S63)

\[ |u_{R,p1} (k)|^2 + |u_{R,p2} (k)|^2 - |v_{R,p2} (k)|^2 = 1, \]  
(S64)

\[ u_{R,11}^* (k) u_{R,12} (k) + u_{R,21}^* (k) u_{R,22} (k) - v_{R,11}^* (k) v_{R,12} (k) - v_{R,21}^* (k) v_{R,22} (k) = 0, \]  
(S65)

\[ u_{R,11} (k) u_{R,21}^* (k) + u_{R,12} (k) u_{R,22}^* (k) - v_{R,11} (k) v_{R,12}^* (k) - v_{R,21} (k) v_{R,22}^* (k) = 0, \]  
(S66)

\[ u_{R,12} (k) v_{R,11}^* (k) + u_{R,22} (k) v_{R,21}^* (k) - u_{R,11} (k) v_{R,12}^* (k) - u_{R,21} (k) v_{R,22}^* (k) = 0, \]  
(S67)

and

\[ u_{R,21} (k) v_{R,11} (k) + u_{R,22} (k) v_{R,12} (k) - u_{R,11} (k) v_{R,21} (k) - u_{R,12} (k) v_{R,22} (k) = 0. \]  
(S68)

For simplicity, we concentrate on a stable system where every term in Eq. (S40) is real. From Eq. (S64),

\[ u_{R,p1} (k) = \frac{\{ \tilde{\omega}_a (k) + \tilde{\omega}_p (k) \} |A_{14} (k)| \sqrt{\tilde{\omega}_a^2 (k)}}{\sqrt{\tilde{\omega}_p (k) [4\tilde{\omega}_a (k) \tilde{\omega}_a^2 (k) + \{ \tilde{\omega}_a^2 (k) - \tilde{\omega}_p^2 (k) \}^2]}}. \]  
(S69)
\( u_{R,p_2}(k) = -\text{sign}\{A_{14}(k)\} \frac{\{\bar{\omega}_{a2}(k) + \bar{\omega}_p(k)\} \{\omega_{a1}^2(k) - \omega_p^2(k)\}}{2\sqrt{\bar{\omega}_{a2}(k) \bar{\omega}_p(k) \left[4\bar{\omega}_{a1}(k) \bar{\omega}_{a2}(k) A_{14}^2(k) + \{\omega_{a1}^2(k) - \omega_p^2(k)\}^2\right]}}, \) (S70)

\( v_{R,p_1}(k) = \frac{\{\bar{\omega}_{a1}(k) - \bar{\omega}_p(k)\} |A_{14}(k)| \sqrt{\bar{\omega}_{a2}(k)}}{\sqrt{\bar{\omega}_p(k) \left[4\bar{\omega}_{a1}(k) \bar{\omega}_{a2}(k) A_{14}^2(k) + \{\omega_{a1}^2(k) - \omega_p^2(k)\}^2\right]}}, \) (S71)

and

\( v_{R,p_2}(k) = -\text{sign}\{A_{14}(k)\} \frac{\{\bar{\omega}_{a2}(k) - \bar{\omega}_p(k)\} \{\omega_{a1}^2(k) - \omega_p^2(k)\}}{2\sqrt{\bar{\omega}_{a2}(k) \bar{\omega}_p(k) \left[4\bar{\omega}_{a1}(k) \bar{\omega}_{a2}(k) A_{14}^2(k) + \{\omega_{a1}^2(k) - \omega_p^2(k)\}^2\right]}}. \) (S72)

From Eq. [S46], \( u_{p_1}(k) = \cos \phi(k) u_{R,p_1}(k) - \sin \phi(k) u_{R,p_2}(k) \), \( u_{p_2}(k) = \sin \phi(k) u_{R,p_1}(k) + \cos \phi(k) u_{R,p_2}(k) \), \( v_{p_1}(k) = \cos \phi(k) v_{R,p_1}(k) - \sin \phi(k) v_{R,p_2}(k) \), and \( v_{p_2}(k) = \sin \phi(k) v_{R,p_1}(k) + \cos \phi(k) v_{R,p_2}(k) \).

As we already pointed out below Eq. [S46], signs of \( \cos \phi(k) \) and \( \sin \phi(k) \) do not change the Bogoliubov conditions in Eqs. [S22] and [S23]. Thus, we will choose signs such that \( u_{p_1}(k) \geq 0 \) for all \( k > 0 \). Then we get

\( u_{p_1}(k) = \sqrt{\frac{u_{R,p_1}^2(k) + u_{R,p_2}^2(k) + \{u_{R,p_1}^2(k) - u_{R,p_2}^2(k)\} \cos \{2\phi(k)\} - 2u_{R,p_1}(k) u_{R,p_2}(k) \sin \{2\phi(k)\}}{2}}, \) (S73)

\( u_{p_2}(k) = \sqrt{\frac{u_{R,p_1}^2(k) + u_{R,p_2}^2(k) - \{u_{R,p_1}^2(k) - u_{R,p_2}^2(k)\} \cos \{2\phi(k)\} + 2u_{R,p_1}(k) u_{R,p_2}(k) \sin \{2\phi(k)\}}{2}} \times \text{sign} \left[ 2u_{R,p_1}(k) u_{R,p_2}(k) \cos \{2\phi(k)\} + \{u_{R,p_1}^2(k) - u_{R,p_2}^2(k)\} \sin \{2\phi(k)\} \right], \) (S74)

\( v_{p_1}(k) = \sqrt{\frac{v_{R,p_1}^2(k) + v_{R,p_2}^2(k) + \{v_{R,p_1}^2(k) - v_{R,p_2}^2(k)\} \cos \{2\phi(k)\} - 2v_{R,p_1}(k) v_{R,p_2}(k) \sin \{2\phi(k)\}}{2}} \times \text{sign} \left[ u_{R,p_1}(k) v_{R,p_1}(k) + u_{R,p_2}(k) v_{R,p_2}(k) + \{u_{R,p_1}(k) v_{R,p_1}(k) - u_{R,p_2}(k) v_{R,p_2}(k)\} \cos \{2\phi(k)\} \right], \) (S75)

and

\( v_{p_2}(k) = \sqrt{\frac{v_{R,p_1}^2(k) + v_{R,p_2}^2(k) - \{v_{R,p_1}^2(k) - v_{R,p_2}^2(k)\} \cos \{2\phi(k)\} + 2v_{R,p_1}(k) v_{R,p_2}(k) \sin \{2\phi(k)\}}{2}} \times \text{sign} \left[ u_{R,p_1}(k) v_{R,p_1}(k) - u_{R,p_2}(k) v_{R,p_1}(k) + \{u_{R,p_1}(k) v_{R,p_2}(k) + u_{R,p_2}(k) v_{R,p_1}(k)\} \cos \{2\phi(k)\} \right], \) (S76)

where \( \tan \{2\phi(k)\} = 2\bar{\omega}_c(k) - \bar{\omega}_d(k) \). For small \( k \) limit,

\( u_{11}(k) = \sqrt{\frac{1 - 2y^2}{2\sqrt{k}}} \left( B_2 - \frac{B_3}{4|A_1|} \right)^{1/4} + O\left(\sqrt{k}\right), \quad u_{12}(k) = -\frac{y}{\sqrt{k}} \left( B_2 - \frac{B_3}{4|A_1|} \right)^{1/4} + O\left(\sqrt{k}\right), \) (S77)

\( v_{11}(k) = -\text{sign}\{1 - 6y^2\} \sqrt{\frac{1 - 2y^2}{2\sqrt{k}}} \left( B_2 - \frac{B_3}{4|A_1|} \right)^{1/4} + O\left(\sqrt{k}\right), \quad v_{12}(k) = \frac{y}{\sqrt{k}} \left( B_2 - \frac{B_3}{4|A_1|} \right)^{1/4} + O\left(\sqrt{k}\right), \) (S78)
### III. REACTION RATE OPERATOR

In the Heisenberg picture, let \( \dot{N}_j (t) := \int d^3 r \dot{\psi}_j \dot{(r, t)} \dot{\psi}_j (r, t) \) where \( j = a, m \). From Eqs. \((S1)\), we get

\[
 i\hbar \frac{\partial \dot{N}_a (t)}{\partial t} = \int d^3 r \left\{ \psi_a^\dagger (r, t) \left( i\hbar \frac{\partial \dot{\psi}_a (r, t)}{\partial t} \right) - \mathrm{h.c.} \right\} = \alpha \sqrt{2} \int d^3 r \left\{ \psi_a^\dagger (r, t) \dot{\psi}_a (r, t) \dot{\psi}_m (r, t) - \mathrm{h.c.} \right\},
\]

or

\[
 -2i\hbar \frac{\partial \dot{N}_m (t)}{\partial t}. \tag{S79}
\]

We define the dimensionless reaction rate operator \( \dot{R} (t) \) by

\[
 \dot{R} (t) := \frac{\hbar}{g_{an}} \frac{\partial \dot{N}_a (t)}{\partial t} = \frac{\partial \dot{N}_a (t)}{\partial t} = \hat{i} \frac{\alpha \sqrt{2}}{g_{an}} \int d^3 r \left\{ \dot{\psi}_a (r, t) \psi_a (r, t) \dot{\psi}_m (r, t) - \mathrm{h.c.} \right\}, \tag{S80}
\]

where \( \hat{i} := g_{an} \hat{t} / \hbar \) is dimensionless time. If \( \langle \psi_R | \hat{R} (t) | \psi_R \rangle \neq 0 \) for some state \( | \psi_R \rangle \), then that state describes reaction between atoms and molecules.

For a homogeneous system with \( V_a (r, t) = 0 \) and \( V_m (r, t) = 0 \), by writing

\[
 \dot{\psi}_a (r, t) = e^{-i\mu t/\hbar} \left\{ x \sqrt{N} e^{i\varphi_a} + \frac{1}{\sqrt{V}} \sum_{k \neq 0} e^{ikr} \delta \dot{\psi}_a (k, t) \right\}, \quad \dot{\psi}_m (r, t) = e^{-2i\mu t/\hbar} \left\{ y \sqrt{N} e^{i\varphi_m} + \frac{1}{\sqrt{V}} \sum_{k \neq 0} e^{ikr} \delta \dot{\psi}_m (k, t) \right\}. \tag{S81}
\]

The reaction rate operator \( \dot{R} (t) \) can be written as

\[
 \dot{R} (t) = 2N \alpha x^2 y \sin \varphi_{am} \left[ -2i\alpha x \sum_{k \neq 0} \left\{ e^{-i\varphi_a} \delta \dot{\psi}_a^\dagger (k, t) \delta \dot{\psi}_m (k, t) - e^{i\varphi_m} \delta \dot{\psi}_a (k, t) \delta \dot{\psi}_m^\dagger (k, t) \right\} 
\right.
\]

\[
 -i\alpha y \sum_{k \neq 0} \left\{ e^{i\varphi_m} \delta \dot{\psi}_a^\dagger (k, t) \delta \dot{\psi}_a (-k, t) - e^{-i\varphi_m} \delta \dot{\psi}_a (k, t) \delta \dot{\psi}_a (-k, t) \right\} 
\]

\[
 -i \frac{\alpha}{\sqrt{V}} \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \left\{ \delta \dot{\psi}_a^\dagger (k_1, t) \delta \dot{\psi}_a (k_2, t) \delta \dot{\psi}_m (k_1 + k_2, t) - \delta \dot{\psi}_a (k_1, t) \delta \dot{\psi}_a (k_2, t) \delta \dot{\psi}_m^\dagger (k_1 + k_2, t) \right\}, \tag{S82}
\]

where \( V \) is the volume of the system. Now, let

\[
 \dot{R}_2 (t) := -2i\alpha x \sum_{k \neq 0} \left\{ e^{-i\varphi_a} \delta \dot{\psi}_a^\dagger (k, t) \delta \dot{\psi}_m (k, t) - e^{i\varphi_m} \delta \dot{\psi}_a (k, t) \delta \dot{\psi}_m^\dagger (k, t) \right\} 
\]

\[
 -i\alpha y \sum_{k \neq 0} \left\{ e^{i\varphi_m} \delta \dot{\psi}_a^\dagger (k, t) \delta \dot{\psi}_a (-k, t) - e^{-i\varphi_m} \delta \dot{\psi}_a (k, t) \delta \dot{\psi}_a (-k, t) \right\} 
\]

\[
 = -i\alpha \sum_{k \neq 0} \left[ \delta \dot{\psi}_a^\dagger (k, t) \delta \dot{\psi}_m (k, t) \delta \dot{\psi}_a (-k, t) \delta \dot{\psi}_m (-k, t) \right] \left[ \begin{array}{cc} M_{R,1} & M_{R,2} \\ -M_{R,2} & -M_{R,1} \end{array} \right] 
\]

\[
 \delta \dot{\psi}_a (k, t) \delta \dot{\psi}_m (k, t) \delta \dot{\psi}_a (-k, t) \delta \dot{\psi}_m (-k, t) \right], \tag{S83}
\]

where

\[
 M_{R,1} := \left[ \begin{array}{cc} 0 & xe^{-i\varphi_a} \\ -xe^{i\varphi_a} & 0 \end{array} \right], \quad M_{R,2} := \left[ \begin{array}{cc} ye^{i\varphi_m} & 0 \\ 0 & 0 \end{array} \right], \tag{S84}
\]

and \( x^2 + 2y^2 = 1 \) from the number conservation in Eq. \((2)\).

Inserting Eqs. \((S20)\) into Eq. \((S83)\), one can get

\[
 \dot{R}_2 (t) = -i\alpha \sum_{k \neq 0} \left[ \delta \psi_1^\dagger (k, t) \delta \psi_2^\dagger (k, t) \delta \psi_1 (-k, t) \delta \psi_2 (-k, t) \right] M_{R,B} (k) \left[ \begin{array}{c} \delta \psi_1 (k, t) \\ \delta \psi_2 (k, t) \\ \delta \psi_1 (-k, t) \\ \delta \psi_2 (-k, t) \end{array} \right], \tag{S85}
\]
where

\[ M_{R,B}(k) := \begin{bmatrix} U(k) & V(k) \\ V^T(k) & U^T(k) \end{bmatrix} \begin{bmatrix} M_{R,1} & M_{R,2} \\ -M_{R,2} & -M_{R,1} \end{bmatrix} \begin{bmatrix} U(k) & V^*(k) \\ V^T(k) & U^*(k) \end{bmatrix}. \]  

(S86)

After some lengthy calculations, one can show that \( M_{R,B} \) can be written as

\[ M_{R,B}(k) = \begin{bmatrix} M_{R,B;1}(k) & M_{R,B;2}(k) \\ -M_{R,B;2}(k) & -M_{R,B;1}(k) \end{bmatrix}, \]

where

\[ M_{R,B;1}(k) := U^\dagger(k) M_{R,1} U(k) - V^\dagger(k) M_{R,1}^* V(k) + U^\dagger(k) M_{R,2} V(k) - V^\dagger(k) M_{R,2}^* U(k), \]

(S87)

and

\[ M_{R,B;2}(k) := U^\dagger(k) M_{R,1} V^*(k) - V^\dagger(k) M_{R,1}^* U^*(k) + U^\dagger(k) M_{R,2}^* U(k) - V^\dagger(k) M_{R,2}^* V(k). \]

(S88)

Since \( M_{R,1}^\dagger = -M_{R,1} \) and \( M_{R,2}^\dagger = M_{R,2}^\dagger = M_{R,B} \). Thus, we may write

\[ M_{R,B;1}(k) = \left[ \begin{array}{cc} \Xi_{11}(k) & \Xi_{12}(k) \\ -\Xi_{12}^*(k) & \Xi_{22}(k) \end{array} \right], \quad M_{R,B;2}(k) = \left[ \begin{array}{cc} \Xi_{13}(k) & \Xi_{14}(k) \\ \Xi_{14}^*(k) & \Xi_{24}(k) \end{array} \right], \]

(S90)

with \( \Xi_{\zeta_{\zeta}}(k) \) being purely imaginary (\( \zeta = 1, 2 \)) as \( M_{R,B;1}(k) = -M_{R,B;1}(k) \) and \( M_{R,B;2}(k) = M_{R,B;2}(k) \).

Thus, Eq. (S85) can be written as

\[
\hat{R}_2(t) = \bar{\alpha} \sum_{k \neq 0} \text{Im} \{\Xi_{11}(k)\} \left\{ 2b_1^\dagger(k, t) b_1(k, t) + 1 \right\} + \bar{\alpha} \sum_{k \neq 0} \text{Im} \{\Xi_{22}(k)\} \left\{ 2b_2^\dagger(k, t) b_2(k, t) + 1 \right\} - 2i\bar{\alpha} \sum_{k \neq 0} \Xi_{12}(k) b_1^\dagger(k, t) b_2(k, t) - h.c. - i\bar{\alpha} \sum_{k \neq 0} \Xi_{13}(k) b_1^\dagger(k, t) b_1^\dagger(-k, t) - h.c. + 2i\bar{\alpha} \sum_{k \neq 0} \Xi_{14}(k) b_1^\dagger(k, t) b_2^\dagger(-k, t) - h.c. - i\bar{\alpha} \sum_{k \neq 0} \Xi_{24}(k) b_2^\dagger(k, t) b_2^\dagger(-k, t) - h.c. .
\]

(S91)

Since we set \( \cos \varphi_{am} = -\text{sign}(\alpha), \) \( \sin \varphi_{am} = 0 \) and \( \hat{R}(t) = \hat{R}_2(t) + O(\bar{\delta}\bar{\Psi}_j^2) \). We also imposed \( \varphi_a = 0 \) below Eq. (S18), which leads to

\[
\Xi_{pp}(k) = 2i\sqrt{1 - 2\gamma^2} \left\{ u_{R,p1}(k) u_{R,p2}(k) - u_{R,p1}^*(k) u_{R,p2}(k) \right\} - \text{sign}(\alpha) \gamma \text{Im} \left\{ u_{R,p1}(k) v_{R,p1}(k) + u_{R,p2}(k) v_{R,p2}(k) \right\} - \text{sign}(\alpha) \gamma \text{Im} \left\{ u_{R,p1}(k) v_{R,p1}(k) - u_{R,p2}(k) v_{R,p2}(k) \right\} \cos(2\phi(k)) - \left\{ u_{R,p1}(k) v_{R,p2}(k) + u_{R,p2}(k) v_{R,p1}(k) \right\} \sin(2\phi(k)), \]

(S92)

\[
\Xi_{12}(k) = \sqrt{1 - 2\gamma^2} \left\{ u_{R,11}(k) u_{R,22}(k) - v_{R,11}(k) v_{R,22}(k) - u_{R,12}(k) u_{R,21}(k) + v_{R,12}(k) v_{R,21}(k) \right\} - \text{sign}(\alpha) \frac{\gamma}{2} \left\{ u_{R,11}(k) v_{R,21}(k) - u_{R,21}(k) v_{R,11}(k) + u_{R,12}(k) v_{R,22}(k) - u_{R,22}(k) v_{R,12}(k) \right\} - \text{sign}(\alpha) \frac{\gamma}{2} \left\{ u_{R,11}(k) v_{R,21}(k) - u_{R,21}(k) v_{R,11}(k) - u_{R,12}(k) v_{R,22}(k) + u_{R,22}(k) v_{R,12}(k) \right\} \cos(2\phi(k)) + \text{sign}(\alpha) \frac{\gamma}{2} \left\{ u_{R,11}(k) v_{R,22}(k) + u_{R,12}(k) v_{R,21}(k) - u_{R,21}(k) v_{R,12}(k) - u_{R,22}(k) v_{R,11}(k) \right\} \sin(2\phi(k)), \]

(S93)

\[
\Xi_{13}(k) = 2\sqrt{1 - 2\gamma^2} \left\{ u_{R,11}(k) v_{R,12}(k) - u_{R,12}(k) v_{R,11}(k) \right\} - \text{sign}(\alpha) \frac{\gamma}{2} \left\{ \left( u_{R,11}(k) \right)^2 + \left( u_{R,12}(k) \right)^2 - \left( v_{R,11}(k) \right)^2 - \left( v_{R,12}(k) \right)^2 \right\} \cos(2\phi(k)) + \text{sign}(\alpha) \frac{\gamma}{2} \left\{ \left( u_{R,11}(k) \right)^2 - \left( u_{R,12}(k) \right)^2 - \left( v_{R,11}(k) \right)^2 + \left( v_{R,12}(k) \right)^2 \right\} \sin(2\phi(k)), \]

(S94)
The quantum mechanical nature of this average rate is manifest in the third line, containing the squeezing parameter where the displacement and squeezing operators read
\[ \hat{b}_1(k,t) \text{ and } \hat{s}_1(k) \]
For low temperatures, \( 0 \leq (\alpha U(k), V(k)) \) are all real, from Eqs. \( \text{(S92)}, \text{(S93)}, \text{(S94)}, \text{(S95)} \), and \( (S96), \Xi_{pp}(k) = 0 \) and \( \Xi_{pq}(k) \in \mathbb{R} \) for \( p \neq q \).

For low temperatures, \( 0 \leq \hbar \omega_1(k) < \hbar \omega_2(k) \), the massive reactants are frozen out and the system is to good approximation in Bogoliubov mode 1 (states purely created by \( \hat{b}_1(k,t) \)). \( \hat{R}_2(t) \) in Eq. \( \text{(S91)} \) then simplifies as
\[ \hat{R}_2(t) = -i\alpha \sum_{k \neq 0} \Xi_{13}(k) \left\{ b_1^\dagger(k,t) b_1^\dagger(-k,t) - h.c. \right\}. \]  

We now present examples of the vacuum expectation values of \( \hat{R}(t) \) for two quantum-mechanical reaction states.

(a) We define the squeezed coherent state as \( |\beta_1(k_1, t), \zeta (k_1)\rangle := \hat{D}(\beta_1(k_1, t)) \hat{D}(\beta_1(-k_1, t)) \hat{s}(\zeta (k_1)) |\text{vac}\rangle \), where the displacement and squeezing operators read \( \hat{D}(\beta_1(k, t)) := e^{i\beta_1(k,t)\hat{b}_1(k,t) - \beta_1^*(k,t)\hat{b}_1^\dagger(k,t)} \) and \( \hat{s}(\zeta (k)) := e^{i\zeta(k)\hat{b}_1^\dagger(k,t)\hat{b}_1(-k,t) - \zeta^*(k)\hat{b}_1(k,t)\hat{b}_1^\dagger(-k,t)} \), respectively. Here, \( |\text{vac}\rangle \) represents the reactant quasi-particle vacuum at initial time \( t = 0 \) where \( \hat{b}_p(k,0)|\text{vac}\rangle = 0 \). Since \( \hat{b}_p(k,t) = e^{-i\omega_0(k)t}\hat{b}_p(k,0) \) from our Hamiltonian in Eq. \( [5] \), we get \( \hat{b}_p(k, t)|\text{vac}\rangle = 0 \) for all \( t \). With \( |\text{vac}\rangle \), we obtain the reaction rate (to \( O(\delta\hat{\Psi}^3) \))
\[ \langle \beta_1(k_1, t), \zeta (k_1) | \hat{R}(t) | \beta_1(k_1, t), \zeta (k_1) \rangle |\text{squeezed state} = 2\alpha \Xi_{13}(k_1) \left[ 2\text{Im} \{ \beta_1^*(k_1, t) \beta_1^*(\zeta (k_1)) \} + \sinh (2 |\zeta (k_1)|) \text{Im} \{ \zeta^*(k_1) / |\zeta (k_1)| \} \right]. \]  
The quantum mechanical nature of this average rate is manifest in the third line, containing the squeezing parameter \( \zeta (k_1) \).

(b) A reactant pair state may be defined as
\[ |\psi_{s,1}(k_1, t)\rangle := \frac{1 + e^{i\theta(k_1)}b_1^\dagger(k_1,t)b_1(-k_1,t)}{\sqrt{2}} |\text{vac}\rangle, \]  
where \( \theta(k_1) \) is the phase of the excited pair relative to the vacuum. Then the reaction rate turns out to be
\[ \langle \psi_{s,1}(k_1, t) | \hat{R}(t) | \psi_{s,1}(k_1, t) \rangle |\text{reaction pair} = -2\alpha \Xi_{13}(k_1) \sin \theta(k_1) + O(\delta\hat{\Psi}^3), \]  
displaying the factor \( \propto \sin \theta(k_1) \), which is due to quantum interference.

IV. SMALL PERTURBATIONS AND HAMILTONIAN BILINEARIZATION

In the Schrödinger picture, let the time dependent bilinear Hamiltonian be \( \hat{H}_S(t) \) where
\[ \hat{H}_S(t) = \hbar \sum_{k \neq 0} \left\{ \omega_1(k) b_1^\dagger(k) \hat{b}_1(k) + \omega_2(k) b_2^\dagger(k) \hat{b}_2(k) \right\} + \hat{V}_S(t), \]
and
\[ \hat{V}_S(t) = V_{ex} f(t) \sum_{k \neq 0} \left\{ \mathcal{V}_1(k) b_1^\dagger(k) \hat{b}_1(k) + \mathcal{V}_2(k) b_1^\dagger(k) \hat{b}_2(k) \right\}. \]
a small perturbation. Here, \( V_{ex}, f(t), \) and \( \mathcal{V}_1(k) \) are real and \( f(t) = 0 \) for \( t < 0 \) so that our Hamiltonian is a time-independent operator at \( t < 0 \). We assume a small perturbation, i.e. \( 0 \leq V_{ex} \ll \hbar \omega_1(k) \) for \( k \neq 0 \), and also assume that the Bogoliubov excitation energies \( \omega_1(k) \) and \( \omega_2(k) \) are real and positive so that the system is in a stable state. For simplicity, let \( \omega_1(k) \ll \omega_2(k) \) so that one may neglect effects of \( b_2(k) \).

To solve this perturbation problem with time dependent perturbation \( \hat{V}_S(t) \), we use the interaction picture instead of the Heisenberg picture. Let \( \hat{H}_{0,S} := \hbar \sum_{k \neq 0} \omega_1(k) b_1^\dagger(k) b_1(k) \). By denoting states in Schrödinger picture as \( |\psi_S(t)\rangle \), states in interaction picture as \( |\psi_I(t)\rangle := \hat{U}_0(t) |\psi_S(t)\rangle \) where \( \hat{U}_0(t) := \exp \left( i \hat{H}_{0,S} t / \hbar \right) \), and the time evolution operator as \( \hat{U}_I(t) \) where \( |\psi_I(t)\rangle = \hat{U}_I(t) |\psi_I(0)\rangle \), \( \partial / \partial t \hat{U}_I(t) = \hat{V}_I(t) \hat{U}_I(t) \) where \( \hat{V}_I(t) := \hat{U}_0(t) \hat{V}_S(t) \hat{U}_0^\dagger(t) \), we get

\[
\hat{U}_I(t) = 1 - \frac{i}{\hbar} \int_0^t dt_1 \hat{V}_I(t_1) - \frac{1}{\hbar^2} \int_0^t dt_1 \hat{V}_I(t_1) \int_0^{t_1} dt_2 \hat{V}_I(t_2) + O \left( \hat{V}_I^3(t) \right). \tag{S103}
\]

With our \( \hat{H}_{0,S}, \hat{U}_0(t) b_1(k) \hat{U}_0^\dagger(t) = e^{-i \omega_1(k)t} b_1(k) \) and hence the time evolution operator \( \hat{U}_I(t) \) is

\[
\hat{U}_I(t) = 1 - 2 \hat{V}_{ex}^2 \sum_{k \neq 0} T_{2,-,+} (k, k, \tilde{t}) |\mathcal{V}_2(k)|^2
\]

\[
- i \hat{V}_{ex} \sum_{k \neq 0} \left[ T_{1,0} (\tilde{t}) \mathcal{V}_1(k) - i \hat{V}_{ex} \left( T_{2,0,0} (\tilde{t}) \mathcal{V}_2^2(k) + 4 T_{2,-,+} (k, k, \tilde{t}) |\mathcal{V}_2(k)|^2 \right) \right] b_1^\dagger(k) b_1(k)
\]

\[
- i \hat{V}_{ex} \sum_{k \neq 0} \left[ T_{1,+} (k, \tilde{t}) - 2 i \hat{V}_{ex} T_{2,0,+} (k, \tilde{t}) \mathcal{V}_1(k) \right] \mathcal{V}_2(k) b_1^\dagger(k) b_1(-k)
\]

\[
- i \hat{V}_{ex} \sum_{k \neq 0} \left[ T_{1,-} (k, \tilde{t}) - 2 i \hat{V}_{ex} T_{2,-,0} (k, \tilde{t}) \mathcal{V}_1(k) \right] \mathcal{V}_2(k) b_1(k) b_1(-k)
\]

\[
- \hat{V}_{ex}^2 T_{2,0,0} (\tilde{t}) \sum_{k_1 \neq 0, k_2 \neq 0} \mathcal{V}_1^2 (k_1) \mathcal{V}_1^2 (k_2) b_1^\dagger (k_1) b_1^\dagger (k_2) b_1 (k_2) b_1 (k_1)
\]

\[
- \hat{V}_{ex}^2 \sum_{k_1 \neq 0, k_2 \neq 0} \left\{ T_{2,+,-} (k_1, k_2, \tilde{t}) + T_{2,-,+} (k_2, k_1, \tilde{t}) \right\} \mathcal{V}_2 (k_1) \mathcal{V}_2^* (k_2) b_1^\dagger (k_1) b_1^\dagger (-k_1) b_1 (k_2) b_1 (-k_2)
\]

\[
- \hat{V}_{ex}^2 \sum_{k_1 \neq 0, k_2 \neq 0} \left\{ T_{2,-,0} (k_1, \tilde{t}) + T_{2,0,-} (k_1, \tilde{t}) \right\} \mathcal{V}_2 (k_1) \mathcal{V}_2 (k_2) b_1^\dagger (k_1) b_1^\dagger (-k_1) b_1 (k_2) b_1 (-k_2)
\]

\[
- \hat{V}_{ex}^2 \sum_{k_1 \neq 0, k_2 \neq 0} \sum_{k_3 \neq 0} T_{2,+,+} (k_1, k_2, \tilde{t}) \mathcal{V}_2 (k_1) \mathcal{V}_2 (k_2) b_1^\dagger (k_1) b_1^\dagger (-k_1) b_1 (k_2) b_1 (-k_2)
\]

\[
- \hat{V}_{ex}^2 \sum_{k_1 \neq 0, k_2 \neq 0} \sum_{k_3 \neq 0} T_{2,-,-} (k_1, k_2, \tilde{t}) \mathcal{V}_2^* (k_1) \mathcal{V}_2^* (k_2) b_1 (k_1) b_1 (k_2) b_1 (-k_1) b_1 (-k_2)
\]

where \( \hat{V}_{ex} := V_{ex} / (g a n) \) and \( \tilde{t} := g a n t / \hbar \). By introducing \( \tilde{\omega}_1(k) := \hbar \omega_1(k) / (g a n) \), we get

\[
T_{1,0} (\tilde{t}) := \int_0^\tilde{t} d\tilde{t}_1 f (\tilde{t}_1), \quad T_{1,\pm} (k_1, \tilde{t}) := \int_0^\tilde{t} d\tilde{t}_1 e^{\pm i \tilde{\omega}_1 (k_1) \tilde{t}_1} f (\tilde{t}_1), \quad T_{2,0,0} (\tilde{t}) := \int_0^\tilde{t} d\tilde{t}_1 f (\tilde{t}_1) \int_0^{\tilde{t}_1} d\tilde{t}_2 f (\tilde{t}_2), \tag{S105}
\]

\[
T_{2,\pm,0} (k, \tilde{t}) := \int_0^\tilde{t} d\tilde{t}_1 e^{\pm i \tilde{\omega}_1 (k) \tilde{t}_1} f (\tilde{t}_1) \int_0^{\tilde{t}_1} d\tilde{t}_2 f (\tilde{t}_2), \quad T_{2,0,\pm} (k, \tilde{t}) := \int_0^\tilde{t} d\tilde{t}_1 f (\tilde{t}_1) \int_0^{\tilde{t}_1} d\tilde{t}_2 e^{\pm i \tilde{\omega}_1 (k) \tilde{t}_2} f (\tilde{t}_2), \tag{S106}
\]

\[
T_{2,\pm,+} (k_1, k_2, \tilde{t}) := \int_0^\tilde{t} d\tilde{t}_1 e^{\pm i \tilde{\omega}_1 (k_1) \tilde{t}_1} f (\tilde{t}_1) \int_0^{\tilde{t}_1} d\tilde{t}_2 e^{2i \tilde{\omega}_1 (k_2) \tilde{t}_2} f (\tilde{t}_2), \tag{S107}
\]

and
\[
T_{2,\pm,\mp} (k_1, k_2, \tilde{\i}) := \int_0^\tilde{\i} d\tilde{\i}_1 e^{\pm 2i\omega_1 (k_1) \tilde{\i}_1} f (\tilde{\i}_1) \int_0^{\tilde{\i}_1} d\tilde{\i}_2 e^{-2i\omega_1 (k_2) \tilde{\i}_2} f (\tilde{\i}_2).
\] (S108)

With this perturbation, in the interaction picture, the initial Bogoliubov vacuum state |vac⟩ is propagated as

\[
|\Psi_0 (t)⟩ = \hat{U}_I (t) |\text{vac}\rangle
= \left\{ 1 - \hat{V}_{ex}^2 \psi_{0,2} (\tilde{t}) \right\} |\text{vac}\rangle - i\hat{V}_{ex} \sum_{k \neq 0} \left\{ \psi_{2,1} (k, \tilde{t}) - i\hat{V}_{ex} \psi_{2,2} (k, \tilde{t}) \right\} \hat{V}_2 (k) |k, -k⟩ \\
- \hat{V}_{ex}^2 \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \psi_{4,2} (k_1, k_2, \tilde{t}) \hat{V}_2 (k_1) \hat{V}_2 (k_2) |k_1, -k_1, k_2, -k_2⟩ + O \left( \hat{V}_{ex}^3 \right),
\] (S109)

where

\[
\psi_{0,2} (\tilde{t}) = 2 \sum_{k \neq 0} T_{2,-,\pm} (k, k, \tilde{t}) |\hat{V}_2 (k)|^2, \quad \psi_{2,1} (k, \tilde{t}) = T_{1,\pm} (k, \tilde{t}), \quad \psi_{2,2} (k, \tilde{t}) = 2T_{2,0,+} (k, \tilde{t}) \hat{V}_1 (k),
\]
\[
\psi_{4,2} (k_1, k_2, \tilde{t}) = T_{2,\pm,\pm} (k_1, k_2, \tilde{t}),
\] (S110)

\[
|k, -k⟩ \equiv \hat{b}_1^\dagger (k) \hat{b}_1^\dagger (-k) |\text{vac}\rangle, \quad |k_1, -k_1, k_2, -k_2⟩ \equiv \hat{b}_1^\dagger (k_1) \hat{b}_1^\dagger (-k_1) \hat{b}_1^\dagger (k_2) \hat{b}_1^\dagger (-k_2) |\text{vac}\rangle, \quad \text{and}
\]
\[
|k_1, -k_1, k_2, -k_2, k_3, -k_3⟩ \equiv \hat{b}_1^\dagger (k_1) \hat{b}_1^\dagger (-k_1) \hat{b}_1^\dagger (k_2) \hat{b}_1^\dagger (-k_2) \hat{b}_1^\dagger (k_3) \hat{b}_1^\dagger (-k_3) |\text{vac}\rangle.
\]

With this state, the reaction rate is

\[
\langle \hat{R}_2 (t) \rangle = -2\alpha \sum_{k \neq 0} \Xi_{13} (k) \text{Im} \left\{ e^{-2i\omega_1 (k) \tilde{t}} \langle \Psi_0 (t) | \hat{b}_1^\dagger (k) \hat{b}_1^\dagger (-k) |\Psi_0 (t)⟩ \right\}
= 4\alpha \hat{V}_{ex} \sum_{k \neq 0} \Xi_{13} (k) \text{Im} \left\{ e^{-2i\omega_1 (k) \tilde{t}} \psi_{2,1}^\dagger (k, \tilde{t}) \hat{V}_2 (k) \right\} + O \left( \hat{V}_{ex}^2 \right).
\] (S111)

When measuring \( \hat{V}_{ex} \), using formula in [53] and Eq. (S109), the quantum Fisher information \( I_Q (\hat{V}_{ex}, \tilde{t}) \) is

\[
I_Q (\hat{V}_{ex}, \tilde{t}) = 8 \sum_{k \neq 0} |\psi_{2,1} (k, \tilde{t})|^2 |\hat{V}_2 (k)|^2 + O \left( \hat{V}_{ex}^3 \right).
\] (S112)

Let \( P_0 (t) = |\langle \Psi_0 (t) |\text{vac}\rangle|^2 \) and \( P_2 (t) = (1/2) \sum_{k \neq 0} |\langle \Psi_0 (t) | k, -k⟩|^2 \) (note that \( |k, -k⟩ = | -k, k⟩ \) from our definition below Eqs. (S110)). Then

\[
P_0 (t) = 1 - 2\hat{V}_{ex}^2 \text{Re} \left\{ \psi_{0,2} (\tilde{t}) \right\} + O \left( \hat{V}_{ex}^3 \right), \quad P_2 (t) = 2\hat{V}_{ex}^2 \sum_{k \neq 0} |\psi_{2,1} (k, \tilde{t}) \hat{V}_2 (k)|^2 + O \left( \hat{V}_{ex}^3 \right),
\] (S113)

and \( \langle \Psi_0 (t)|\Psi_0 (t)⟩ = P_0 (t) + P_2 (t) + O \left( \hat{V}_{ex}^3 \right). \) Note that \( I_Q (\hat{V}_{ex}, \tilde{t}) = 4P_2 (t)/\hat{V}_{ex}^2 + O \left( \hat{V}_{ex}^3 \right). \)

Now, suppose that we want to measure \( \hat{M} \) with the state initially in Bogoliubov vacuum where \( \hat{M}_S = \sum_{k \neq 0} \left\{ \hat{M}_{1} (k) + \hat{M}_{2} (k) \hat{b}_1^\dagger (k) \hat{b}_1^\dagger (-k) + \hat{M}_{3} (k) \hat{b}_1^\dagger (k) \hat{b}_1^\dagger (-k) \right\} \) in the Schrödinger picture. In the interaction picture, by denoting \( \hat{M}_I (t) := \hat{U}_0 (t) \hat{M}_S \hat{U}_0^\dagger (t) \), we get
\[
\hat{M}_f (\tilde{t}) | \hat{\Psi}_0 (\tilde{t}) \rangle = \sum_{k \neq 0} \left[ M_1 (k) - 2 \hat{V}_{ex} e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,1} (k, \tilde{t}) M_3^* (k) V_2 (k) - \hat{V}_{ex}^2 \right] | \psi_{2,1} (\tilde{t}) \rangle M_1 (k) + 2 e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,2} (k, \tilde{t}) M_5^* (k) V_2 (k) \right] | \text{vac} \rangle \\
+ \sum_{k_1 \neq 0} e^{2i\tilde{\omega}_1 (k_1) \tilde{t}} M_3 (k) - i \hat{V}_{ex} \psi_{2,1} (k, \tilde{t}) \left\{ 2M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} V_2 (k) \\
+ \left\{ 2M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} V_2 (k) \\
- \hat{V}_{ex} \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} e^{2i\tilde{\omega}_1 (k_1, k_2) \tilde{t}} \psi_{2,1} (k_1, \tilde{t}) \left\{ M_3 (k_1) + \psi_{2,2} (k_1, k_2, \tilde{t}) \sum_{k_3 \neq 0} M_1 (k_3) \right\} \psi_{2,2} (k_2, \tilde{t}) \right\} \left\{ M_3 (k_1) + \psi_{2,2} (k_1, k_2, \tilde{t}) \sum_{k_3 \neq 0} M_1 (k_3) \right\} \psi_{2,2} (k_2, \tilde{t}) \right\} \left\{ M_3 (k_1) + \psi_{2,2} (k_1, k_2, \tilde{t}) \sum_{k_3 \neq 0} M_1 (k_3) \right\} \psi_{2,2} (k_2, \tilde{t}) \\
- \hat{V}_{ex}^2 \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \sum_{k_3 \neq 0} e^{2i\tilde{\omega}_1 (k_1, k_2, k_3) \tilde{t}} \psi_{4,2} (k_1, k_2, \tilde{t}) \left\{ M_3 (k_1, k_2) \psi_{2,2} (k_2, \tilde{t}) \right\} \left\{ M_3 (k_1, k_2) \psi_{2,2} (k_2, \tilde{t}) \right\} \left\{ M_3 (k_1, k_2) \psi_{2,2} (k_2, \tilde{t}) \right\} \left\{ M_3 (k_1, k_2) \psi_{2,2} (k_2, \tilde{t}) \right\} + O \left( \hat{V}_{ex}^3 \right), \\
(S114)
\]

\[
\langle \hat{\Psi}_0 (\tilde{t}) | \hat{M}_f (\tilde{t}) | \hat{\Psi}_0 (\tilde{t}) \rangle = \sum_{k \neq 0} M_1 (k) + 4 \hat{V}_{ex} \sum_{k \neq 0} \text{Im} \left\{ e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,1} (k, \tilde{t}) M_3^* (k) V_2 (k) \right\} + O \left( \hat{V}_{ex}^3 \right) \\
+ \hat{V}_{ex}^2 \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \left\{ V_2 (k) \right\} \left\{ M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} - 2 \text{Re} \left\{ \psi_{2,2} (\tilde{t}) \right\} M_1 (k) - 4 \text{Re} \left\{ e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,2} (k, \tilde{t}) M_3^* (k) V_2 (k) \right\} \\
(S115)
\]

and

\[
\langle \hat{\Psi}_0 (\tilde{t}) | \hat{M}_f^2 (\tilde{t}) | \hat{\Psi}_0 (\tilde{t}) \rangle = \left\{ \sum_{k \neq 0} M_1 (k) \right\}^2 + 2 \sum_{k \neq 0} \left\{ M_3 (k) \right\}^2 + 8 \hat{V}_{ex} \sum_{k \neq 0} \sum_{k_1 \neq 0} \left\{ M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} \text{Im} \left\{ e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,1} (k, \tilde{t}) M_3^* (k) V_2 (k) \right\} \\
+ 4 \sum_{k \neq 0} e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,1} (k, \tilde{t}) M_3^* (k) V_2 (k) \left\{ \sum_{k \neq 0} \left\{ 2M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} \psi_{2,2} (k, \tilde{t}) \right\}^2 + \sum_{k \neq 0} \left\{ 2M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} \psi_{2,2} (k, \tilde{t}) \right\}^2 \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\}^2 \\
+ 8 \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\}^2 \left\{ \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\} \right\}^2 + \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \left\{ \sum_{k_1 \neq 0} M_1 (k_1) \right\} \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\}^2 \\
+ 2 \hat{V}_{ex}^2 \left\{ \sum_{k \neq 0} \left\{ \sum_{k_1 \neq 0} M_1 (k_1) \right\} \right\}^2 + 2 \sum_{k \neq 0} \left\{ \sum_{k_1 \neq 0} \left\{ M_3 (k) \right\} \right\}^2 \left\{ \sum_{k \neq 0} \left\{ \sum_{k_1 \neq 0} M_1 (k_1) \right\} \right\} - 2 \sum_{k \neq 0} \left\{ \sum_{k_1 \neq 0} M_1 (k_1) \right\} \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\} \left\{ \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \right\} \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\} \left\{ \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \right\} \left\{ \sum_{k \neq 0} \left\{ M_3 (k) \right\} \right\} \left\{ \sum_{k \neq 0} \left\{ 2 \psi_{2,1} (k, \tilde{t}) \right\} \right\} \\
+ O \left( \hat{V}_{ex}^3 \right). \\
(S116)
\]

Let
\[
\left\langle \hat{M} (k, \tilde{t}) \right\rangle := \text{Im} \left\{ e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,1} (k, \tilde{t}) M_3^* (k) V_2 (k) \right\} \text{ and } \\
\left\langle \hat{M} (k, \tilde{t}) \right\rangle := 2 \left\{ \psi_{2,1} (k, \tilde{t}) \right\} \left\{ V_2 (k) \right\} \left\{ 2M_2 (k) + \sum_{k_1 \neq 0} M_1 (k_1) \right\} - 2 \text{Re} \left\{ \psi_{2,2} (\tilde{t}) \right\} M_1 (k) - 4 \text{Re} \left\{ e^{-2i\tilde{\omega}_1 (k) \tilde{t}} \psi_{2,2} (k, \tilde{t}) M_3^* (k) V_2 (k) \right\} \\
(S117)
Then the lower bound of the Fisher information $I_C \left( \tilde{V}_{ex, \hat{t}} \right)$ when measuring $\tilde{V}_a$ is

$$I_C \left( \tilde{V}_{ex, \hat{t}} \right) = 8 \left\{ \sum_{k \neq 0} \left( \hat{M} (k, \hat{t}) \right) \right\}^2 + \tilde{V}_{ex} \left[ \sum_{k \neq 0} \left( \hat{M} (k, \hat{t}) \right) \left( \hat{M} (k, \hat{t}) \right) \right]^{''} \left( \sum_{k \neq 0} \left( \hat{M} (k, \hat{t}) \right) \right)^{''} \left( \sum_{k \neq 0} \left| M_3 (k) \right|^2 \right)^2 \left( \sum_{k \neq 0} \left| M_3 (k) \right|^2 \right) \left( \sum_{k \neq 0} \left| M_3 (k) \right|^2 \right) + O \left( \tilde{V}_{ex} \right) \right)$$

(S118)

To summarize,

$$I_Q \left( \tilde{V}_{ex, \hat{t}} \right) = 8 \sum_{k \neq 0} \left| e^{-2i\omega_1 (k) \hat{t}} \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right|^2 \left| \Psi_2 (k) \right|^2 + O \left( \tilde{V}_{ex} \right)$$

$$I_C \left( \tilde{V}_{ex, \hat{t}} \right) = 8 \sum_{k \neq 0} \left| e^{-2i\omega_1 (k) \hat{t}} \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right|^2 \left| M_3 (k) \right|^2 + O \left( \tilde{V}_{ex} \right)$$

(S119)

where

$$\Re \left\{ e^{-2i\omega_1 (k) \hat{t}} \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} = \Re \left\{ \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} \cos \left\{ 2\omega_1 (k) \hat{t} \right\} + \Im \left\{ \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} \sin \left\{ 2\omega_1 (k) \hat{t} \right\}$$

$$\Im \left\{ e^{-2i\omega_1 (k) \hat{t}} \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} = \Im \left\{ \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} \cos \left\{ 2\omega_1 (k) \hat{t} \right\} - \Re \left\{ \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} \sin \left\{ 2\omega_1 (k) \hat{t} \right\}$$

(S120)

Suppose that $f \left( t \right) = \delta \left( t - t_p \right)$ for $t \geq 0$ (assuming $t_p \geq 0$). Then

$$\Re \left\{ e^{-2i\omega_1 (k) \hat{t}} \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} = \theta \left( \hat{t} - \hat{t}_p \right) \cos \left\{ 2\omega_1 (k) \left( \hat{t} - \hat{t}_p \right) \right\}$$

$$\Im \left\{ e^{-2i\omega_1 (k) \hat{t}} \int_0^\hat{t} dt_1 e^{2i\omega_1 (k) t_1} f \left( \hat{t}_1 \right) \right\} = -\theta \left( \hat{t} - \hat{t}_p \right) \sin \left\{ 2\omega_1 (k) \left( \hat{t} - \hat{t}_p \right) \right\}$$

(S121)

where $\theta \left( \hat{t} \right) = 0$ if $\hat{t} < 0$ and 1 otherwise, and thus

$$I_Q \left( \tilde{V}_{ex, \hat{t}} \right) = 8 \theta \left( \hat{t} - \hat{t}_p \right) \sum_{k \neq 0} \left| \Psi_2 (k) \right|^2 + O \left( \tilde{V}_{ex} \right)$$

$$I_C \left( \tilde{V}_{ex, \hat{t}} \right) = 8 \theta \left( \hat{t} - \hat{t}_p \right) \frac{\sum_{k \neq 0} \left[ \Re \left\{ M_3^* (k) \Psi_2 (k) \right\} \sin \left\{ 2\omega_1 (k) \left( \hat{t} - \hat{t}_p \right) \right\} - \Im \left\{ M_3^* (k) \Psi_2 (k) \right\} \cos \left\{ 2\omega_1 (k) \left( \hat{t} - \hat{t}_p \right) \right\} \right] \right)^2 \sum_{k \neq 0} \left| M_3 (k) \right|^2 + O \left( \tilde{V}_{ex} \right)$$

(S122)
Note that \( I_Q (\tilde{V}_{ex}, \tilde{t}) \) is constant in scaled time \( \tilde{t} \) for \( \tilde{t} \geq \tilde{t}_p \).

If \( f(t) = \theta(t - t_p) \) for \( t \geq 0 \) (assuming \( t_p \geq 0 \)).

\[
\begin{align*}
\text{Re} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \int_0^\tilde{t} dt_1 e^{2i\hat{\omega}_1(k)t_1} f(t_1) \right\} &= \theta(\tilde{t} - \tilde{t}_p) \frac{\sin \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\}}{\hat{\omega}_1 (k)} \cos \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\}, \\
\text{Im} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \int_0^\tilde{t} dt_1 e^{2i\hat{\omega}_1(k)t_1} f(t_1) \right\} &= -\theta(\tilde{t} - \tilde{t}_p) \frac{\sin \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\}}{\hat{\omega}_1 (k)} \sin \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\},
\end{align*}
\]

(S123)

and thus

\[
\begin{align*}
I_Q \left( \tilde{V}_{ex}, \tilde{t} \right) &= 8 \theta(\tilde{t} - \tilde{t}_p) \sum_{k \neq 0} \frac{\sin^2 \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\}}{\hat{\omega}_1^2 (k)} |V_2 (k)|^2 + O \left( \tilde{V}_{ex} \right), \\
I_C \left( \tilde{V}_{ex}, \tilde{t} \right) &= 8 \theta(\tilde{t} - \tilde{t}_p) \sum_{k \neq 0} \frac{\sin \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\}}{\hat{\omega}_1 (k)} \left[ \text{Re} \left\{ M_3^* (k) V_2 (k) \right\} \sin \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\} - \text{Im} \left\{ M_3^* (k) V_2 (k) \right\} \cos \left\{ \hat{\omega}_1 (k) (\tilde{t} - \tilde{t}_p) \right\} \right] \\
&\quad + O \left( \tilde{V}_{ex} \right).
\end{align*}
\]

(S124)

If \( f(t) = \cos (\omega_n t + \delta_n) \) for \( t \geq 0 \),

\[
\begin{align*}
I_Q \left( \tilde{V}_{ex}, \tilde{t} \right) &= 8 \sum_{k \neq 0} |e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t})|^2 |V_2 (k)|^2 + O \left( \tilde{V}_{ex} \right), \\
I_C \left( \tilde{V}_{ex}, \tilde{t} \right) &= 8 \sum_{k \neq 0} \text{Im} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t}) \right\} \text{Re} \left\{ M_3^* (k) V_2 (k) \right\} + \text{Re} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t}) \right\} \text{Im} \left\{ M_3^* (k) V_2 (k) \right\} \\
&\quad + O \left( \tilde{V}_{ex} \right),
\end{align*}
\]

(S125)

where

\[
\begin{align*}
\text{Re} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t}) \right\} &= \frac{\cos \delta_n \sin \left\{ \hat{\omega}_a + \epsilon (k) \right\} \tilde{t}}{2 \hat{\omega}_a + \epsilon (k)} + \frac{\hat{\omega}_a \cos \left\{ \hat{\omega}_a + \epsilon (k) \right\} \tilde{t} + \delta_a \left\{ \hat{\omega}_a + \epsilon (k) \right\}}{2 \hat{\omega}_a + \epsilon (k)} \frac{\sin \left\{ \epsilon (k) \tilde{t} / 2 \right\}}{\epsilon (k) / 2},
\end{align*}
\]

(S126)

\[
\begin{align*}
\text{Im} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t}) \right\} &= \frac{\cos \delta_n \cos \left\{ \hat{\omega}_a + \epsilon (k) \right\} \tilde{t} - \cos \left\{ \hat{\omega}_a \tilde{t} + \delta_a \right\}}{2 \hat{\omega}_a + \epsilon (k)} - \frac{\hat{\omega}_a \sin \left\{ \hat{\omega}_a + \epsilon (k) \right\} \tilde{t} + \delta_a \left\{ \hat{\omega}_a + \epsilon (k) \right\}}{2 \hat{\omega}_a + \epsilon (k)} \frac{\sin \left\{ \epsilon (k) \tilde{t} / 2 \right\}}{\epsilon (k) / 2},
\end{align*}
\]

(S127)

\( \hat{\omega}_a := \omega_a / (ga_n) \), and \( \epsilon (k) := 2\hat{\omega}_1 (k) - \hat{\omega}_a \). Note that both \( \text{Im} \left\{ e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t}) \right\} \) and \( e^{-2i\hat{\omega}_1(k)\tilde{t}} \psi_{2,1} (k, \tilde{t}) \) do not diverge at \( 2\hat{\omega}_1 (k) = \hat{\omega}_a \) (where \( \epsilon (k) = 0 \)).

From now on, we focus on measuring the number of created molecules where \( \hat{M}_S = \int d^3r \delta \hat{\psi}_{in}^\dagger (r) \delta \hat{\psi}_{in} (r) \). Since we neglected effects of \( \hat{b}_2 (k) \),

\[
\hat{M}_S = \sum_{k \neq 0} \left\{ v_{12}^2 (k) + \left\{ u_{12}^2 (k) + v_{12}^2 (k) \right\} \hat{b}_1^\dagger (k) \hat{b}_1 (k) + u_{12} (k) v_{12} (k) \left\{ \hat{b}_1^\dagger (k) \hat{b}_1^\dagger (-k) + \hat{b}_1 (k) \hat{b}_1 (-k) \right\} \right\},
\]

(S128)

where we get \( M_3 (k) = u_{12} (k) v_{12} (k) \), which is real in the stable system.
A. Density Perturbation

Neglecting effects of \( \hat{b}_2 (k) \) (for a system with large gap between \( \omega_1 (k) \) and \( \omega_2 (k) \)), when we perturb the mass densities of the atoms and molecules in the state, i.e., when we impose \( \tilde{V}_S (t) = (V_{ex}/m_n) f (t) \int d^3 r \left\{ m_n \hat{\psi}_n^\dagger (r) \hat{\psi}_n (r) + m_m \hat{\psi}_m^\dagger (r) \hat{\psi}_m (r) \right\} \) with \( m_m \approx 2m_n \), we get

\[
\tilde{V}_S (t) = V_{ex} f (t) \left( N + \sum_{k \neq 0} \left\{ u_{11}^2 (k) + 2u_{12}^2 (k) + \left\{ u_{11}^2 (k) + v_{11}^2 (k) + 2u_{12}^2 (k) + 2v_{12}^2 (k) \right\} \hat{b}_1^\dagger (k) \hat{b}_1 (k) \right\} \\
+ V_{ex} f (t) \sum_{k \neq 0} \left\{ u_{11} (k) v_{11} (k) + 2u_{12} (k) v_{12} (k) \right\} \left\{ \hat{b}_1^\dagger (k) \hat{b}_1^\dagger (-k) + \hat{b}_1 (k) \hat{b}_1 (-k) \right\},
\]

(S129)

which makes \( V_2 (k) = u_{11} (k) v_{11} (k) + 2u_{12} (k) v_{12} (k) \).

B. Density Perturbation on Purely Atomic BEC

For scalar BEC, it is known that \[54\]

\[
\omega_1 (k) = k \xi_n \left( k \xi_n \right)^2 + 2, \quad u_{11} (k) = \sqrt{\frac{1}{2} \left( \frac{(k \xi_n)^2 + 1}{\omega_1 (k)} \right) + 1}, \quad \text{and} \quad v_{11} (k) = -\sqrt{\frac{1}{2} \left( \frac{(k \xi_n)^2 + 1}{\omega_1 (k)} \right) - 1}. \quad (S130)
\]

Note that in the Heisenberg picture with purely atomic BEC, Eqs. (S131), (S29), and (S29) can be written as

\[
\delta \hat{\psi}_n (r, t) = e^{-i \int dt V_n (r, t)/\hbar e^{-i \mu t/\hbar}} \sum_{k \neq 0} B (r, k) \left\{ u_{11} (k) \hat{b}_1 (k, t) + v_{11}^* (k) \hat{b}_1^\dagger (-k, t) \right\}, \quad B (r, k) = \frac{1}{\sqrt{V}} e^{i k \cdot r}, \quad (S131)
\]

where the \( B (r, k) \) span an orthonormal basis of the single-particle Hilbert space that satisfies \[d^3 r \int \delta \hat{\psi}_n (r, k) \delta \hat{\psi}_n^\dagger (r, k) = \delta_{k_1, k_2}.\]

When \( f (t) = \sin (\omega_1 t) \), from Eqs. (S125), (S126), and (S127), we get

\[
I_Q \left( \tilde{V}_{ex}, t \right) \rightarrow 4t^2 \left| u_{11} (k_r) v_{11} (k_r) \right|^2 = \left| 2 g_n \frac{t}{\hbar} u_{11} (k_r) v_{11} (k_r) \right|^2 \quad \text{for} \quad t \gg 1,
\]

(S132)

where \( \omega_1 (k_r) = \omega_n / 2 \) (Remember that we define \( \omega_1 (k) := \omega_1 (k) / (g_n n) \), \( \hat{\lambda} := g_n \mu t / \hbar \), and \( V_{ex} := \sqrt{V} V_{ex} / (g_n n) \) in the main text). For \( V_{ex} = (m_n/2) \left( L^2 / 12 \right) \) (our approximation of the density perturbation due to gravitational wave in Eq. (7)), we get

\[
I_Q (G, t) = \left( \frac{\partial \tilde{V}_{ex}}{\partial G} \right)^2 I_Q (\tilde{V}_{ex}, t) \rightarrow \left| \frac{2 \sqrt{V}}{\sqrt{G}} \frac{t}{\hbar} u_{11} (k_r) v_{11} (k_r) \right|^2 \quad \text{for} \quad t \gg 1.
\]

(S133)

For \( \tilde{V}_S (t) = \sin (\omega_n t) \int d^3 r \left\{ m_n G r_t^2 / 2 \right\} \hat{\psi}_n^\dagger (r) \hat{\psi}_n (r) \) where \( r = \sum_{j=1}^{3} r_j e_j \) (\( e_j \) are Cartesian basis vectors), \[14\] independently calculated \( I_Q (G, t) \) for a quasi-1D system with \( -L/2 < r_1 < L/2 \) and \( t \gg 1 \) by taking \( B (r, k) = \sqrt{2/(AL)} \cos (k_{n_1} (r_1 + L/2)) \) with \( k_{n_1} = n_1 \pi / L \) (\( n_1 \) are positive integers). Their results for mode \( k_r \) where \( \omega_1 (k_r) = \omega_n / 2 \) can be written as

\[
I_Q (G, \hat{t}) \rightarrow \left| 2 \int d^3 r \frac{m_n}{2} G r_t^2 B^* (r, k_r) u_{11}^* (k_r) B (r, k_r) v_{11} (k_r) \right|^2 \\
\rightarrow \left| 2 \left\{ \frac{m_n}{2} \int d^3 r G r_t^2 B^* (r, k_r) B (r, k_r) \right\} \frac{t}{\hbar} u_{11} (k_r) v_{11} (k_r) \right|^2.
\]

(S134)

One can see that Eq. (S134) becomes Eq. (S133) if one takes \( B (r, k) = \left( 1/\sqrt{V} \right) e^{i k \cdot r} \) as we do. Since BEC atoms are confined in \( -L/2 < r_1 < L/2 \), \( \delta \hat{\psi}_n (r, t) \) should be zero at \( r_1 = \pm L/2 \) and our choice of \( B (r, k) \) can satisfy this condition by taking \( k \rightarrow (2\pi / L) e_1 \) which make \( B ((-L/2, r_2, r_3), k) = B ((L/2, r_2, r_3), k) \).
Suppose that the Hamiltonian $\tilde{H}_S(t)$ in Schrödinger picture is given as $\tilde{H}_S(t) = \sum_{k \neq 0} \hat{H}_c(k, t)$. The time evolution operator $\hat{U}_S(t)$ in the Schrödinger picture satisfies $i\hbar \frac{\partial \hat{U}_S(t)}{\partial t} = \hat{H}_S(t) \hat{U}_S(t)$.

From Appendix A of [55], let $\hat{U}_S(t) = \hat{U}_1(t) \hat{U}_2(t) \hat{U}_3(t)$ with $\hat{U}_j(t) = \exp \left\{ -i \sum_{k \neq 0} F_j(k, t) \hat{G}_j(k) \right\}$ for $j = 1, 2, 3$ where $k := |k|$. Then we get

$$\hat{H}_S(t) = \hbar \sum_{k \neq 0} \left\{ \frac{\partial F_1(k, t)}{\partial t} \hat{G}_1(k) + \frac{\partial F_2(k, t)}{\partial t} \hat{G}_2(k) \hat{U}_1^\dagger(t) + \frac{\partial F_3(k, t)}{\partial t} \hat{G}_3(k) \hat{U}_2(t) \hat{U}_3^\dagger(t) \hat{U}_1^\dagger(t) \right\}. \quad (S135)$$

Let $n_b(k)$ be the number of reactions with momentum $k$. From now on, we will denote the state with $n_b(k_j) = n_b(-k_j)$ for all $j$ which satisfy $|k_j| \leq |k_c|$ as $|n_b(k_1), n_b(k_2), \ldots, n_b(k_c)|$ where $k_c$ is the cutoff. By defining

$$\hat{K}_x(k) := \frac{1}{2} \left\{ \hat{b}_1^\dagger(k) \hat{b}_1(k) + \hat{b}_1(-k) \hat{b}_1^\dagger(-k) \right\}, \quad \hat{K}_y(k) := \frac{1}{2} \left\{ \hat{b}_1^\dagger(k) \hat{b}_1^\dagger(-k) + \hat{b}_1(k) \hat{b}_1(-k) \right\},$$

$$\hat{K}_z(k) := \frac{1}{2} \left\{ \hat{b}_1^\dagger(k) \hat{b}_1^\dagger(-k) - \hat{b}_1(k) \hat{b}_1(-k) \right\}, \quad (S136)$$

and $\hat{K}_\pm(k) = \hat{K}_x(k) \pm i\hat{K}_y(k)$, we get $\hat{K}_\zeta(k) = \hat{K}_\zeta(-k)$ for $\zeta = x, y, z, \pm$.

$$\hat{K}_+(k_j) |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c)) = \hat{b}_1^\dagger(k_j) \hat{b}_1^\dagger(-k_j) |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c))$$

$$= \sqrt{n_b(k_j) + 1} \left\{ \begin{array}{l} \text{with } \hat{b}_1^\dagger(k_j) \\ \text{with } \hat{b}_1^\dagger(-k_j) \end{array} \right\} |n_b(k_1), \ldots, n_b(k_j) + 1, \ldots, n_b(k_c)),$$

$$= n_b(k_j) |n_b(k_1), \ldots, n_b(k_j) + 1, \ldots, n_b(k_c)), \quad (S137)$$

and

$$\hat{K}_-(k_j) |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c)) = \hat{b}_1(k_j) \hat{b}_1(-k_j) |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c))$$

$$= \sqrt{n_b(k_j) \sqrt{n_b(k_j)}} |n_b(k_1), \ldots, n_b(k_j) - 1, \ldots, n_b(k_c)),$$

$$= n_b(k_j) |n_b(k_1), \ldots, n_b(k_j) - 1, \ldots, n_b(k_c)), \quad (S138)$$

and

$$\hat{K}_z(k_j) |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c)) = \frac{1}{2} \left\{ \hat{b}_1^\dagger(k_j) \hat{b}_1(k_j) + \hat{b}_1(-k_j) \hat{b}_1^\dagger(-k_j) \right\} |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c))$$

$$= \frac{1}{2} \left\{ \begin{array}{l} n_b(k_j) \\ + \quad n_b(k_j) + 1 \end{array} \right\} |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c))$$

$$= \left\{ n_b(k_j) + \frac{1}{2} \right\} |n_b(k_1), \ldots, n_b(k_j), \ldots, n_b(k_c)). \quad (S139)$$

Therefore, we get

$$|n_b(k_1), \ldots, n_b(k_c)) = \prod_{j=1}^{c} \frac{1}{n_b(k_j)!} \left\{ \hat{K}_+(k_j) \right\}^{n_b(k_j)} |\text{vac}, \quad (S140)$$

where $|\text{vac}$ is Bogoliubov vacuum state.
From now on, for simplicity, we will consider \( \hat{H}_S (t) \) in Eq. \( \text{(S101)} \) and \( \text{(S102)} \) without \( \hat{b}_2 (k) \) terms as we did in section \( \text{IV} \). Additionally, we will assume that \( \nabla_2 (k) \in \mathbb{R} \) like Eq. \( \text{(S129)} \). By choosing \( \hat{G}_1 (k) = \hat{K}_z (k) \), \( \hat{G}_2 (k) = \hat{K}_x (k) \), and \( \hat{G}_3 (k) = \hat{K}_y (k) \), we get

\[
\hat{H}_e (k, t) = \{ \hbar \omega_1 (k) + V_{ex} f (t) \nabla_1 (k) \} \frac{1}{2} \left\{ \hat{b}_1^\dagger (k) \hat{b}_1 (k) + \hat{b}_1 (k) \hat{b}_1^\dagger (k) \right\} + V_{ex} f (t) \nabla_2 (k) \left\{ \hat{b}_1 (k) \hat{b}_1^\dagger (k) - \hat{b}_1 (k) \hat{b}_1 (k) \right\}
\]

\[
= \{ \hbar \omega_1 (k) + V_{ex} f (t) \nabla_1 (k) \} \left[ \hat{K}_z (k) + V_{ex} f (t) \nabla_2 (k) \left\{ \hat{K}_+ (k) + \hat{K}_- (k) \right\} \right],
\]

which leads to

\[
\frac{\partial \{ 2F_1 (k, \tilde{t}) \}}{\partial t} = 2g_1 (k, \tilde{t}) - 4g_2 (k, \tilde{t}) \sin \{ 2F_1 (k, \tilde{t}) \} \tanh \{ 2F_2 (k, \tilde{t}) \}, \quad \frac{\partial \{ 2F_2 (k, \tilde{t}) \}}{\partial t} = 4g_2 (k, \tilde{t}) \cos \{ 2F_1 (k, \tilde{t}) \},
\]

\[
\frac{\partial \{ 2F_3 (k, \tilde{t}) \}}{\partial t} = -4g_2 (k, \tilde{t}) \sin \{ 2F_1 (k, \tilde{t}) \} / \cosh \{ 2F_2 (k, \tilde{t}) \},
\]

and

\[
\frac{\partial \{ 2F_1 (k, \tilde{t}) \}}{\partial V_{ex}} = 2 \frac{\partial g_1 (k, \tilde{t})}{\partial V_{ex}} - 4 \frac{\partial g_2 (k, \tilde{t})}{\partial V_{ex}} \sin \{ 2F_1 (k, \tilde{t}) \} \tanh \{ 2F_2 (k, \tilde{t}) \}
\]

\[
-4g_2 (k, \tilde{t}) \cos \{ 2F_1 (k, \tilde{t}) \} \tanh \{ 2F_2 (k, \tilde{t}) \} \frac{\partial \{ 2F_2 (k, \tilde{t}) \}}{\partial V_{ex}} - 4g_2 (k, \tilde{t}) \cosh \frac{4}{2} \frac{\partial \{ 2F_2 (k, \tilde{t}) \}}{\partial V_{ex}},
\]

\[
\frac{\partial \{ 2F_2 (k, \tilde{t}) \}}{\partial V_{ex}} = 4 \frac{\partial g_2 (k, \tilde{t})}{\partial V_{ex}} \cos \{ 2F_1 (k, \tilde{t}) \} - 4g_2 (k, \tilde{t}) \sin \{ 2F_1 (k, \tilde{t}) \} \frac{\partial \{ 2F_2 (k, \tilde{t}) \}}{\partial V_{ex}},
\]

\[
\frac{\partial \{ 2F_3 (k, \tilde{t}) \}}{\partial V_{ex}} = -4 \frac{\partial g_2 (k, \tilde{t})}{\partial V_{ex}} \sin \{ 2F_1 (k, \tilde{t}) \} \cosh \{ 2F_2 (k, \tilde{t}) \} \frac{\partial \{ 2F_1 (k, \tilde{t}) \}}{\partial V_{ex}} - 4g_2 (k, \tilde{t}) \sin \frac{\partial \{ 2F_2 (k, \tilde{t}) \}}{\partial V_{ex}},
\]

where \( \tilde{t} := \sqrt[1]{\frac{g_a}{\hbar}} \), \( \tilde{\omega}_1 (k) := \hbar \omega_1 (k) / (g_a n) \), \( \tilde{V}_{ex} := V_{ex} / (g_a n) \), \( \tilde{g}_1 (k, \tilde{t}) := \tilde{\omega}_1 (k) + \tilde{V}_{ex} f (\tilde{t}) \nabla_1 (k) \), and \( \tilde{g}_2 (k, t) := \tilde{V}_{ex} f (\tilde{t}) \nabla_2 (k) \).

Note that the operator \( \hat{X} (k) \) in \( \text{(54)} \) satisfies

\[
\prod_{k \neq 0} \left\{ e^{i F_3 (k, t) K_z (k)} e^{i F_2 (k, t) K_z (k)} e^{i F_1 (k, t) K_z (k)} \right\} \hat{X} (k) \prod_{k \neq 0} \left\{ e^{-i F_3 (k, t) K_z (k)} e^{-i F_2 (k, t) K_z (k)} e^{-i F_1 (k, t) K_z (k)} \right\} = \Lambda (k, t) \hat{X} (k),
\]

which gives \( \hat{X} (k) := \langle \hat{X} (k) \rangle = 0 \) for our state \( |\Psi_S (t)\rangle := \hat{U}_S (t) |\text{vac} \rangle \). Here,

\[
\Lambda (k, t) := \begin{bmatrix} \Lambda_{1,1} (k, t) & \Lambda_{1,2} (k, t) & \Lambda_{1,3} (k, t) & \Lambda_{1,4} (k, t) \\ -\Lambda_{1,2} (k, t) & \Lambda_{1,1} (k, t) & \Lambda_{1,4} (k, t) & -\Lambda_{1,3} (k, t) \\ \Lambda_{1,3} (k, t) & -\Lambda_{1,4} (k, t) & \Lambda_{1,1} (k, t) & \Lambda_{1,2} (k, t) \\ -\Lambda_{1,4} (k, t) & \Lambda_{1,3} (k, t) & -\Lambda_{1,2} (k, t) & \Lambda_{1,1} (k, t) \end{bmatrix},
\]

where

\[
\begin{align*}
\Lambda_{1,1} (k, t) &= \cos \{ F_1 (k, t) \} \cosh \{ F_2 (k, t) \} \cosh \{ F_3 (k, t) \} + \sin \{ F_1 (k, t) \} \sinh \{ F_2 (k, t) \} \sinh \{ F_3 (k, t) \}, \\
\Lambda_{1,2} (k, t) &= \sin \{ F_1 (k, t) \} \cosh \{ F_2 (k, t) \} \cosh \{ F_3 (k, t) \} - \cos \{ F_1 (k, t) \} \sin \{ F_2 (k, t) \} \sin \{ F_3 (k, t) \}, \\
\Lambda_{1,3} (k, t) &= -[ \cos \{ F_1 (k, t) \} \cosh \{ F_2 (k, t) \} \sin \{ F_3 (k, t) \} + \sin \{ F_1 (k, t) \} \sin \{ F_2 (k, t) \} \cosh \{ F_3 (k, t) \} ], \\
\Lambda_{1,4} (k, t) &= \sin \{ F_1 (k, t) \} \cosh \{ F_2 (k, t) \} \cosh \{ F_3 (k, t) \} - \cos \{ F_1 (k, t) \} \cosh \{ F_2 (k, t) \} \cos \{ F_3 (k, t) \}.
\end{align*}
\]

Hence, from \( \text{(54)} \), the formal expression of the quantum Fisher information \( I_{Q, \text{exact}} \left( \tilde{V}_{ex}, t \right) \) is

\[
I_{Q, \text{exact}} \left( \tilde{V}_{ex}, t \right) = \frac{1}{4} \sum_{k \neq 0} \text{Tr} \left( \left\{ \frac{\partial \Gamma (k, t)}{\partial V_{ex}} \Gamma^{-1} (k, t) \right\}^2 \right)
\]

where \( \Gamma (k, t) = \Lambda (k, t) \Lambda^T (k, t) \).
Now, let
\[ B_2(k,t) := -\frac{1}{2}M_2(k) \left[ \cosh \{ 2F_2(k,\tilde{t}) \} \sinh \{ 2F_3(k,\tilde{t}) \} + i \sinh \{ 2F_2(k,\tilde{t}) \} \right] \]
\[ + \hat{M}_3(k) \left[ \sin \{ 2F_1(k,t) \} \sinh \{ 2F_2(k,t) \} \sinh \{ 2F_3(k,t) \} + \cos \{ 2F_1(k,t) \} \cosh \{ 2F_3(k,t) \} + i \sin \{ 2F_1(k,t) \} \cosh \{ 2F_2(k,t) \} \right], \quad (S148) \]
and
\[ B_3(k,t) := M_2(k) \cosh \{ 2F_2(k,\tilde{t}) \} \cosh \{ 2F_3(k,\tilde{t}) \} \]
\[ - 2\hat{M}_3(k) \left[ \sin \{ 2F_1(k,t) \} \sinh \{ 2F_2(k,t) \} \cosh \{ 2F_3(k,t) \} + \cos \{ 2F_1(k,t) \} \sinh \{ 2F_3(k,t) \} \right]. \quad (S149) \]
Then we get
\[ \langle \Psi_S(t) | \hat{M}_S | \Psi_S(t) \rangle = \sum_{k \neq 0} \left\{ \hat{M}_1(k) - \frac{1}{2}M_2(k) + \frac{1}{2}B_3(k,t) \right\}, \]
\[ \langle \Psi_S(t) | \hat{M}_S^2 | \Psi_S(t) \rangle = \left\{ \langle \Psi_S(t) | \hat{M}_S | \Psi_S(t) \rangle \right\}^2 + 2 \sum_{k \neq 0} |B_2(k,t)|^2, \quad (S150) \]
and the formal expression of the lower bound of classical Fisher information \( I_{C,\text{exact}}(\tilde{V}_{ex},t) \) is
\[ I_{C,\text{exact}}(\tilde{V}_{ex},t) = \frac{1}{8 \sum_{k \neq 0} |B_2(k,t)|^2} \left\{ \sum_{k \neq 0} \frac{\partial B_3(k,t)}{\partial \tilde{V}_{ex}} \right\}^2. \quad (S151) \]