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PHASE DOUBLING AND ENTANGLEMENT GENERATION IN COHERENT
MATTER-WAVE REACTIONS

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To my friends and family.

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ABSTRACT

Chemical reactions in a statistical ensemble are conventionally regarded as incoherent processes driven by thermodynamics. In the classical regime, reactions are expected to proceed faster at high temperatures and slow to a halt in the zero-temperature limit according to Arrhenius kinetics. In the quantum degenerate regime, where bosonic atoms and molecules form coherent matter waves, reactions are instead described by nonlinear mixing of matter-wave fields, leading to collectively-enhanced reaction rates and coherent amplification. This raises the question: how does the matter-wave phase evolve during a reaction, and how can it influence reaction dynamics? In the quantum regime, the matter-wave phases of the reactants and products are expected to match through wave mixing, analogous to phase matching of photonic fields in nonlinear optics.

We report the observation of phase coherent reaction dynamics of Bose-condensed atoms and molecules near a Feshbach resonance. Using matter wave diffraction with optical lattices, we verify spatial coherence of both reactants and products and observe phase doubling when atomic waves combine into molecular waves - the matter-wave analogue of second-harmonic generation. The diffraction patterns also reveal distinct signatures of entanglement generated between reacting particles as the reaction is initiated. Our observations establish phase coherence and entanglement as two essential features of "quantum many-body chemistry" where macroscopic quantum fields govern the reaction dynamics.

CHAPTER 1

CLASSICAL AND QUANTUM REACTION KINETICS

1.1 Introduction

Molecules, compared to atoms, have richer energy structures owing to their additional internal degrees of freedom [1], providing new opportunities for quantum information processing [2, 3], quantum simulation [4, 5], precision measurements [6] and cold chemistry [7, 8]. For example, the molecule’s internal states can be utilized as qubits or qudits for quantum information processing with coherence times on the scale of seconds [9]. Ultracold polar molecules carry electric dipole moments whose strength and orientation can be tuned with external fields, allowing precise control over long-range dipole–dipole interactions that can be used to engineer exotic many-body phenomena such as quantum droplets [10]. Polyatomic molecules provide a new platform for testing the Standard Model (SM) of particle physics, enabling sensitive measurements of fundamental constants such as the proton-to-electron mass ratio via rovibrational spectroscopy and searches for the electron’s permanent electric dipole moment, whose effects can be strongly enhanced by the large internal electromagnetic fields present within the molecule [11].

In recent years, advances in laser cooling and quantum state manipulation have opened new avenues in the field of cold and ultracold chemistry. Chemical reactions in the classical regime are driven by thermodynamics and follow Arrhenius rate laws. Nevertheless, reactions can still proceed in the zero temperature limit [12], where the wave-like nature of particles becomes more prominent. At ultracold temperatures, reactants occupy a single quantum state and the reaction rate can be controlled through initial state preparation [13, 14]. These developments raise a natural question: how does matter-wave coherence evolve when particles undergo a chemical reaction? The recent realization of Bose–Einstein condensates (BEC) of short-range molecules [15, 16], where a macroscopic ensemble of molecules shares a common

phase, provides an ideal setting to answer this question.

1.2 Reaction mechanisms and classical rate laws

1.2.1 Basics of reaction kinetics

We begin by examining reactions in the classical regime where phase coherence plays no role. Reaction kinetics studies how fast chemical reactions occur and the factors that influence those rates. Many reactions follow a simple rate law

$$v = k[A]^a[B]^b[C]^c, \quad (1.1)$$

where v is the rate, k is the rate constant, $[A]$, $[B]$ and $[C]$ are the molar concentrations, and a , b and c are the reaction orders. For example, in an elementary reaction such as $A + A \rightarrow A_2$, the rate law is $v = k[A]^2$, where the reaction order a equals the stoichiometric coefficient of 2.

The rate constant k is often assumed to follow the Arrhenius equation

$$k = Z \exp(-E_a/RT), \quad (1.2)$$

where Z is the pre-exponential (frequency) factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. The pre-exponential factor depends on collision frequency and proper orientation of the molecules during the collision process, while the activation energy corresponds to the minimum energy required to initiate a reaction. High temperatures and low activation energies makes the rate constant larger, thereby accelerating the reaction. Catalysts can also be used to lower the activation energy and, in some cases, modify the pre-exponential factor. Arrhenius kinetics provide a foundational framework for characterizing chemical reactivity in the thermally activated, classical regime.

1.2.2 Kinetics of dimer association and dissociation

Here, we model an elementary reaction using classical rate laws. The association and dissociation of dimers, $A + A \rightleftharpoons A_2$, are described by the following rate equations

$$\frac{dm}{dt} = k_a n^2 - k_d m \quad (1.3)$$

$$\frac{dn}{dt} = -2k_a n^2 + 2k_d m, \quad (1.4)$$

where $n = N/V$ and $m = M/V$ are the monomer and dimer densities, N and M are the monomer and dimer populations, and V is the volume which is set to unity for convenience. The coefficients $k_a \propto e^{-E_a/k_B T}$ and $k_d \propto e^{-E_d/k_B T}$ are the rate constants for association and dissociation, respectively. Here, E_a and E_d are their corresponding activation energies, and k_B is the Boltzmann constant. The factor of two in Eq. (1.4) are stoichiometric coefficients. By assuming the total number density n_t is conserved, $n_t = n + 2m$, we can rewrite the dimer rate equation as

$$\frac{dm}{dt} = 4k_a m^2 - (4k_a n_t + k_d)m + k_a n_t^2. \quad (1.5)$$

By setting $dm/dt = 0$, we find that

$$4k_a m^2 - (4k_a n_t + k_d)m + k_a n_t^2 = 4k_a(m - m_+)(m - m_-), \quad (1.6)$$

where $m_{\pm} = \frac{1}{8k_a} \left(4k_a n_t + k_d \pm \sqrt{8k_a k_d n_t + k_d^2} \right)$. Substituting Eq. (1.6) into Eq. (1.5) and applying separation of variables, we get

$$\frac{dm}{(m - m_+)(m - m_-)} = 4k_a dt. \quad (1.7)$$

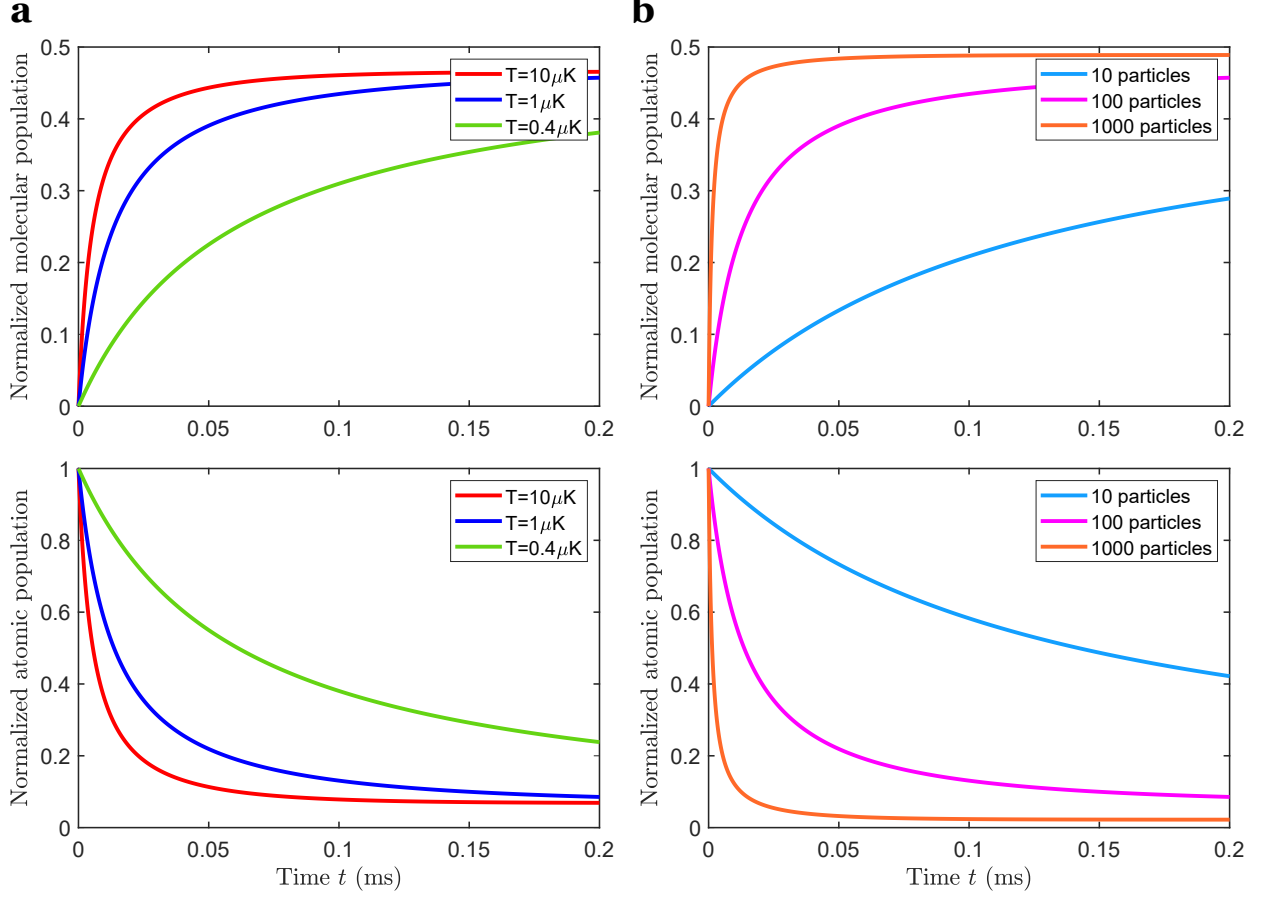


Figure 1.1: **Classical reaction kinetics of dimer association and dissociation.** **a**, Temperature dependence of reaction kinetics. Activation energy is $E_a = k_B \times 1\mu\text{K}$ and total particle number is 100. Lower temperatures lead to slower reaction rates. **b**, Particle-number (density) dependence of reaction kinetics. Activation energy is $E_a = k_B \times 1\mu\text{K}$ and temperature is $T = 1\mu\text{K}$. Higher densities lead to faster reaction rates.

Integrating both sides gives us

$$\frac{4k_a}{R} \ln \left| \frac{m - m_+}{m - m_-} \right| = 4k_a t + K, \quad (1.8)$$

where we used $R = \sqrt{8k_a k_d n_t + k_d^2}$ and K is a constant. When $m(0) = 0$, we get $K = \frac{4k_a}{R} \ln \frac{m_+}{m_-}$. By substituting $K = \frac{4k_a}{R} \ln \frac{m_+}{m_-}$ into Eq. (1.8) and taking the exponent of both sides, we arrive at

$$m(t) = \frac{m_+(1 - e^{Rt})}{1 - (m_+/m_-)e^{Rt}}. \quad (1.9)$$

On the other hand, when we impose the initial condition $m(0) = n_t/2$, the solution becomes

$$m(t) = \frac{m_+(R - k_d) + m_-(R + k_d)e^{Rt}}{R - k_d + (R + k_d)e^{Rt}}. \quad (1.10)$$

From Eqs. (1.9) and (1.10), we find that both monomer and dimer densities reach equilibrium as $t \rightarrow \infty$. These solutions show that the rates at which $m(t)$ and $n(t)$ evolve are set by the total number density n_t and the temperature T , see Fig. 1.1. The reaction rate increases with both number density and temperature as expected from classical collision theory. However, in the opposite limit of ultracold temperatures, the reaction is expected to slow dramatically as thermal activation becomes negligible and long-range scattering physics begin to dominate.

In Fig. 1.1, we set the pre-exponential factor Z to unity to simplify the reaction kinetics. According to hard sphere collision theory, the pre-exponential factor can be defined as

$$Z = n_a n_b N_A^2 d_{ab}^2 \left(\frac{8\pi k_B T}{\mu_{ab}} \right)^{1/2}, \quad (1.11)$$

where n_a and n_b are the moles of the reactants a and b, N_A is Avogadro's constant, $d_{ab} = d_a + d_b$ is sum of the radii of the reacting particles, and $\mu_{ab} = m_a m_b / (m_a + m_b)$ is the reduced mass [17]. In some definitions, the rate constant may be defined as $k = PZ e^{-E_a/k_B T}$ which includes the steric factor P . The steric factor is the probability that a collision occurs with reactants in the correct orientation.

1.3 Nonlinear wave mixing in the quantum degenerate regime

1.3.1 Two-body Feshbach coupling

In the quantum degenerate regime at ultracold temperatures, where bosonic reactants and products constitute *macroscopic quantum fields*, the reaction dynamics are governed by nonlinear wave mixing rather than classical rate laws [18, 19, 20]. The interaction Hamiltonian for the association and dissociation of diatomic molecules near a Feshbach resonance is described by two-body Feshbach coupling

$$H_2 = \hbar\gamma(\hat{\psi}_m^\dagger\hat{\psi}_a^2 + \hat{\psi}_a^{\dagger 2}\hat{\psi}_m), \quad (1.12)$$

where $\hat{\psi}_a$ and $\hat{\psi}_m$ are the field operators for atoms and molecules, respectively, and γ is the Feshbach coupling constant. From this interaction Hamiltonian, we can derive the Heisenberg equations of motion for the field operators $\hat{\psi}_a$ and $\hat{\psi}_m$

$$\frac{d}{dt}\hat{\psi}_a = \frac{i}{\hbar}[\hat{H}_2, \hat{\psi}_a] = -2i\gamma\hat{\psi}_a^\dagger\hat{\psi}_m \quad (1.13)$$

$$\frac{d}{dt}\hat{\psi}_m = \frac{i}{\hbar}[\hat{H}_2, \hat{\psi}_m] = -i\gamma\hat{\psi}_a^2, \quad (1.14)$$

where we used the bosonic commutators $[\hat{\psi}_i, \hat{\psi}_j^\dagger] = \delta_{i,j}$, $[\hat{\psi}_i^\dagger, \hat{\psi}_j^\dagger] = [\hat{\psi}_i, \hat{\psi}_j] = 0$ for $i, j = a, m$.

The total particle number is conserved since

$$\frac{d}{dt}\hat{N}_t = \frac{i}{\hbar}[\hat{H}_2, \hat{N}_t] = 0, \quad (1.15)$$

where $\hat{N}_t = \hat{N} + 2\hat{M} = \hat{\psi}_a^\dagger\hat{\psi}_a + 2\hat{\psi}_m^\dagger\hat{\psi}_m$ is the total number operator. The equations of motion for the number operators $\hat{M}$ and $\hat{N}$ are

$$\frac{d\hat{M}}{dt} = -\frac{1}{2}\frac{d\hat{N}}{dt} = \frac{i}{\hbar}[\hat{H}_2, \hat{M}] = i\gamma(\hat{\psi}_a^{\dagger 2}\hat{\psi}_m - \hat{\psi}_a^2\hat{\psi}_m^\dagger), \quad (1.16)$$

where we used $\frac{d\hat{N}}{dt} + 2\frac{d\hat{M}}{dt} = \frac{d}{dt}\hat{N}_t = 0$. Using mean-field approximation, we replace the field operators with complex amplitudes, $\hat{\psi}_a \rightarrow \sqrt{N}e^{i\varphi_a}$ and $\hat{\psi}_m \rightarrow \sqrt{M}e^{i\varphi_m}$, where φ_a and φ_m are the atomic and molecular phases, respectively. Therefore, we can rewrite Eq. (1.16) as

$$\frac{dM}{dt} = -\frac{1}{2}\frac{dN}{dt} = 2\gamma N\sqrt{M}\sin\varphi_R, \quad (1.17)$$

where $\varphi_R = 2\varphi_a - \varphi_m$ is the reaction angle. We can also derive an equation of motion for φ_R using Eqs. (1.13) and (1.14)

$$\frac{d\varphi_R}{dt} = 2\frac{d\varphi_a}{dt} - \frac{d\varphi_m}{dt} = \gamma\frac{N-4M}{\sqrt{M}}\cos\varphi_R. \quad (1.18)$$

Eqs. (1.17) and (1.18) characterize the coherent dynamics of atom-molecule coupling.

We simplify Eqs. (1.17) and (1.18) as

$$\frac{dM}{dt} = 2\gamma(N_t - 2M)\sqrt{M}\sin\varphi_R \quad (1.19)$$

$$\frac{d\varphi_R}{dt} = \gamma\frac{N_t - 6M}{\sqrt{M}}\cos\varphi_R, \quad (1.20)$$

where N_t is a constant. Taking the ratio of Eqs (1.19) and (1.20) yields

$$\frac{dM}{d\varphi_R} = \frac{2M(N_t - 2M)}{N_t - 6M}\tan\varphi_R. \quad (1.21)$$

By applying separation of variables and integrating both sides, we obtain

$$\frac{1}{2}\ln M + \ln(N_t - 2M) = -\ln\cos\varphi_R + C_0, \quad (1.22)$$

where C_0 is a constant. As a final step, taking the exponent of both sides yields

$$\sqrt{M}(N_t - 2M)\cos\varphi_R = C. \quad (1.23)$$

By imposing the initial condition $M(0) = 0$, we obtain $C = 0$. Hence, Eq. (1.23) only holds for $\varphi_R = \pi/2 \pmod{2\pi}$ or $-\pi/2 \pmod{2\pi}$ when $t > 0$. On the other hand, we also obtain $C = 0$ when $M(0) = N_t/2$ and obtain the same conditions for φ_R .

1.3.2 Molecular association

When the initial condition is $M(0) = 0$, the only physically acceptable solution is $\varphi_R = \pi/2 \pmod{2\pi}$ since $C = 0$. By substituting $\varphi_R = \pi/2$ into Eq. (1.19) and solving the differential equation via separation of variables, we obtain

$$M(t) = \frac{N_t}{2} \tanh^2 \gamma N_t t \quad (1.24)$$

$$N(t) = N_t(1 - \tanh^2 \gamma N_t t). \quad (1.25)$$

These results suggest that the reaction rate increases with particle number, irrespective of temperature – a hallmark of collective enhancement, also known as “quantum superchemistry” [18, 21]. The molecular association rate scales quadratically with particle number, since $\frac{dM}{dt} = \gamma N_t^2 \tanh(\gamma N_t t)(1 - \tanh^2(\gamma N_t t))$.

1.3.3 Molecular dissociation

When the initial condition is $M(0) = N_t/2$, the only physically acceptable solution is $\varphi_R = -\pi/2 \pmod{2\pi}$ since $C = 0$. By substituting $\varphi_R = -\pi/2$ into Eq. (1.19) and solving the differential equation, we obtain

$$M(t) = \frac{N_t}{2} \left(\frac{C' e^{-2\gamma N_t t} - 1}{C' e^{-2\gamma N_t t} + 1} \right)^2 \quad (1.26)$$

$$N(t) = N_t \left[1 - \left(\frac{C' e^{-2\gamma N_t t} - 1}{C' e^{-2\gamma N_t t} + 1} \right)^2 \right], \quad (1.27)$$

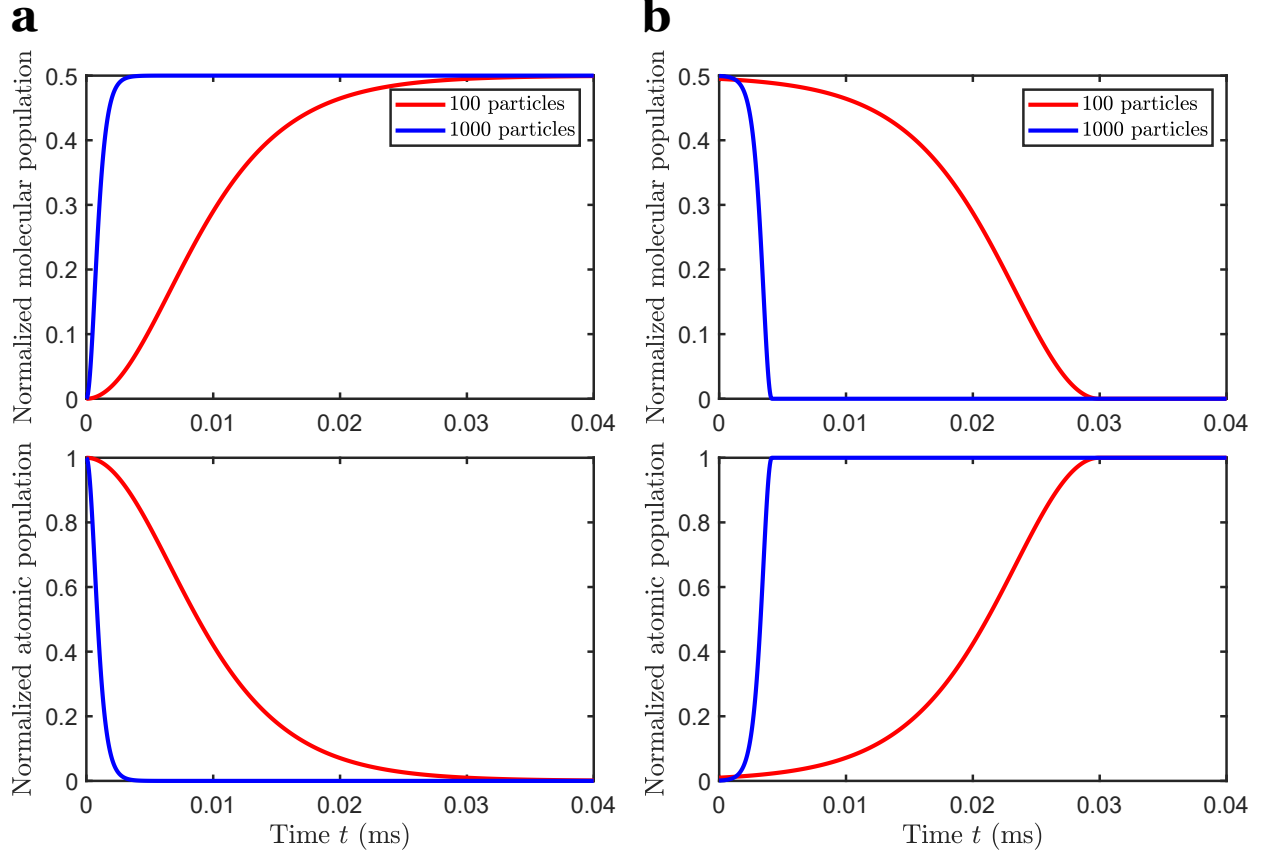


Figure 1.2: **Reaction kinetics in the quantum degenerate regime.** **a**, Molecular association. Association rate scales quadratically with particle number. **b**, Molecular dissociation. Dissociation rate also scales quadratically with particle number. Both processes are temperature-independent.

where $C' = \frac{\sqrt{N_t} + \sqrt{N_t - 1}}{\sqrt{N_t} - \sqrt{N_t - 1}}$. Here, we set the initial condition to $M(0) = N_t/2 - 1$ for $N_t \gg 1$ instead of $M(0) = N_t/2$, because the solution diverges in the latter case. These results also suggest that the dissociation rate is set by the particle number rather than the temperature, consistent with collective enhancement. Here, the molecular dissociation rate also scales quadratically with particle number, since $\frac{dM}{dt} = \frac{-4\gamma N_t^2 C' e^{-2\gamma N_t t} (C' e^{-2\gamma N_t t} - 1)}{(C' e^{-2\gamma N_t t} + 1)^3}$.

1.3.4 Atom-molecule equilibrium

When we set the initial condition to $\varphi_R = 0$, we have $\dot{M} = -\dot{N}/2 = 0$, so both M and N remain constant. Since $\dot{\varphi}_R = \gamma(N_t - 6M)/\sqrt{M} = 0$, we obtain $M = N_t/6$ and $N = 2N_t/3$ at equilibrium.

Near equilibrium, we can linearize the equation of motion to leading order for $M = M_0 + \delta M$ and $\varphi_R = \varphi_{R_0} + \delta\varphi_R$. We expand $\frac{dM}{dt}$ and $\frac{d\varphi_R}{dt}$ as

$$\frac{dM}{dt} = f(M_0, \varphi_{R_0}) + \left. \frac{\partial f}{\partial M} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta M + \left. \frac{\partial f}{\partial \varphi_R} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta\varphi_R + \dots \quad (1.28)$$

$$\frac{d\varphi_R}{dt} = g(M_0, \varphi_{R_0}) + \left. \frac{\partial g}{\partial M} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta M + \left. \frac{\partial g}{\partial \varphi_R} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta\varphi_R + \dots, \quad (1.29)$$

where $f(M, \varphi_R) = 2\gamma(N_t - 2M)\sqrt{M} \sin \varphi_R$ and $g(M, \varphi_R) = \gamma \frac{N_t - 6M}{\sqrt{M}} \cos \varphi_R$. Since $\frac{dM}{dt} = \frac{d}{dt}(M_0 + \delta M) = \frac{d\delta M}{dt}$ and $\frac{d\varphi_R}{dt} = \frac{d}{dt}(\varphi_{R_0} + \delta\varphi_R) = \frac{d\delta\varphi_R}{dt}$ because M_0 and φ_{R_0} are constant, we can simplify Eqs. (1.28) and (1.29) into

$$\frac{dM}{dt} = \left. \frac{\partial f}{\partial M} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta M + \left. \frac{\partial f}{\partial \varphi_R} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta\varphi_R = \frac{4\gamma N_t^{3/2}}{3\sqrt{6}} \delta\varphi_R \quad (1.30)$$

$$\frac{d\varphi_R}{dt} = \left. \frac{\partial g}{\partial M} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta M + \left. \frac{\partial g}{\partial \varphi_R} \right|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \delta\varphi_R = -\frac{6\sqrt{6}\gamma}{\sqrt{N_t}} \delta M, \quad (1.31)$$

where we used $f(M_0, \varphi_{R_0}) = 0$ and $g(M_0, \varphi_{R_0}) = 0$.

Therefore, the linearized system is given by

$$\begin{pmatrix} \frac{dM}{dt} \\ \frac{d\varphi_R}{dt} \end{pmatrix} = \begin{pmatrix} \frac{\partial f}{\partial M} & \frac{\partial f}{\partial \varphi_R} \\ \frac{\partial g}{\partial M} & \frac{\partial g}{\partial \varphi_R} \end{pmatrix} \bigg|_{(M, \varphi_R)=(M_0, \varphi_{R_0})} \begin{pmatrix} \delta M \\ \delta\varphi_R \end{pmatrix} = \begin{pmatrix} 0 & \frac{4\gamma}{3\sqrt{6}} N_t^{3/2} \\ -6\sqrt{6}\gamma N_t^{-1/2} & 0 \end{pmatrix} \begin{pmatrix} \delta M \\ \delta\varphi_R \end{pmatrix}. \quad (1.32)$$

The general solution for these coupled differential equations is

$$\begin{pmatrix} \delta M \\ \delta \varphi_R \end{pmatrix} = e^{Jt} \begin{pmatrix} \delta M(0) \\ \delta \varphi_R(0) \end{pmatrix}, \quad (1.33)$$

where J is the Jacobian

$$J = \begin{pmatrix} 0 & \frac{4\gamma}{3\sqrt{6}} N_t^{3/2} \\ -6\sqrt{6}\gamma N_t^{-1/2} & 0 \end{pmatrix}. \quad (1.34)$$

We evaluate the matrix exponential as $e^{Jt} = V e^{\lambda t} V^{-1}$, where V contains the eigenvectors of the Jacobian and λ is its corresponding diagonal matrix of eigenvalues. This gives us

$$e^{Jt} = V e^{\lambda t} V^{-1} = \begin{pmatrix} \cos(\sqrt{8N_t}\gamma t) & \frac{N_t}{3\sqrt{3}} \sin(\sqrt{8N_t}\gamma t) \\ -\frac{3\sqrt{3}}{N_t} \sin(\sqrt{8N_t}\gamma t) & \cos(\sqrt{8N_t}\gamma t) \end{pmatrix}. \quad (1.35)$$

Thus, the solutions for δM and $\delta \varphi_R$ are

$$\delta M(t) = \delta M(0) \cos(\sqrt{8N_t}\gamma t) + \frac{N_t}{3\sqrt{3}} \delta \varphi_R(0) \sin(\sqrt{8N_t}\gamma t) \approx \delta M(0) \cos(\sqrt{8N_t}\gamma t) \quad (1.36)$$

$$\delta \varphi_R(t) = -\frac{3\sqrt{3}}{N_t} \delta M(0) \sin(\sqrt{8N_t}\gamma t) + \delta \varphi_R(0) \cos(\sqrt{8N_t}\gamma t) \approx -\frac{3\sqrt{3}}{N_t} \delta M(0) \sin(\sqrt{8N_t}\gamma t), \quad (1.37)$$

where we ignore the second terms because $\varphi_R(0) \ll 1$. Furthermore, we use unnormalized eigenvectors since the normalization constant approaches unity for $N_t \gg 1$.

In summary, the equations of motion at equilibrium can be approximated as

$$M(t) = M_0 + \delta M = \frac{N_t}{6} + \delta M(0) \cos(\sqrt{8N_t}\gamma t) \quad (1.38)$$

$$N(t) = N_0 + \delta N = \frac{2}{3}N_t - 2\delta M(0) \cos(\sqrt{8N_t}\gamma t) \quad (1.39)$$

$$\varphi_R(t) = \varphi_{R_0} + \delta\varphi_R = -\frac{3\sqrt{3}}{N_t}\delta M(0) \sin(\sqrt{8N_t}\gamma t) \quad (1.40)$$

From Eqs. (1.38), (1.39) and (1.40), we find that the populations and reaction phase oscillate at frequencies of $\Omega = \gamma\sqrt{8N_t}$ which scales with particle number, consistent with collective enhancement.

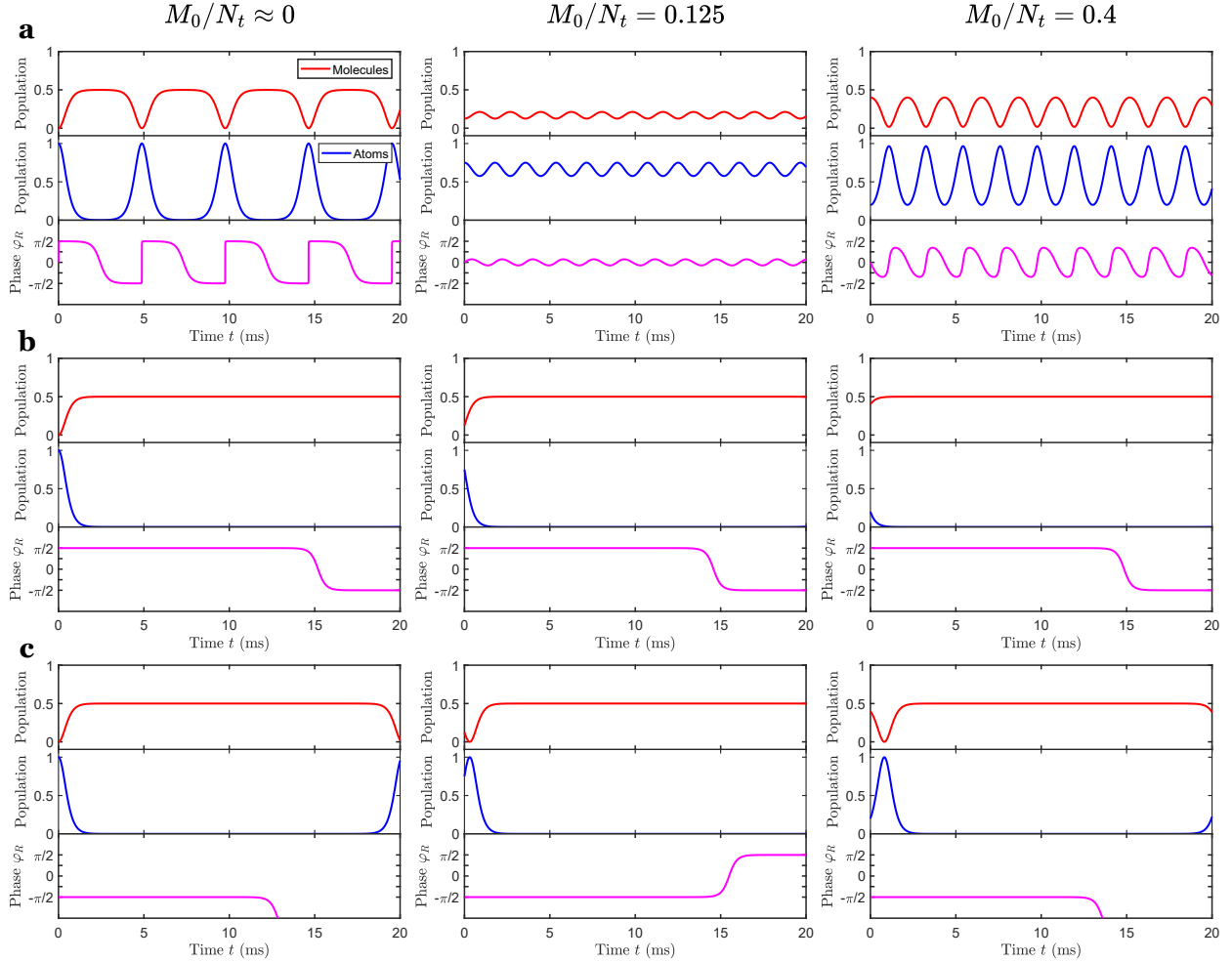


Figure 1.3: **Dynamical solutions of the coupled atom–molecule system.** Numerical solutions of the coupled ODEs in Eqs. (1.19) and (1.20). Here, we plot these solutions with initial conditions of $M_0/N_t \approx 0$, $M_0/N_t = 0.125$ and $M_0/N_t = 0.40$. The Feshbach coupling strength is set to $\gamma = 2\pi \times 6.3$ kHz. **a**, The initial reaction phase is $\varphi_R = 0$. Small amplitude oscillations occur near the equilibrium point of $M_0 = N_t/6$, while large amplitude oscillations occur when the reaction phase flips from $-\pi/2$ to $\pi/2$. **b**, $\varphi_R = \pi/2$. The molecular population saturates while the atomic population decreases to zero. **c**, $\varphi_R = -\pi/2$. The atomic and molecular populations evolve similarly at early times, but exhibit signs of population revival and depletion at later times.

1.3.5 Atom-molecule Hamiltonian with two-body interactions

The atom-molecule Hamiltonian including two-body interactions [22] can be expressed as

$$\begin{aligned}\hat{H} = & \int d\mathbf{x} \hat{\psi}_m^\dagger(\mathbf{x}) \left[-\frac{\hbar^2 \nabla^2}{4m} + \nu \right] \hat{\psi}_m(\mathbf{x}) + \int d\mathbf{x} \hat{\psi}_a^\dagger(\mathbf{x}) \left[-\frac{\hbar^2 \nabla^2}{2m} + \frac{T_{\text{bg}}}{2} \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_a(\mathbf{x}) \right] \hat{\psi}_a(\mathbf{x}) \\ & + \int d\mathbf{x} g \left[\hat{\psi}_m^\dagger(\mathbf{x}) \hat{\psi}_a^2(\mathbf{x}) + \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_m(\mathbf{x}) \right] + \int d\mathbf{x} \frac{T_{\text{mm}}}{2} \hat{\psi}_m^\dagger(\mathbf{x}) \hat{\psi}_m^2(\mathbf{x}) \\ & + \int d\mathbf{x} T_{\text{am}} \hat{\psi}_m^\dagger(\mathbf{x}) \hat{\psi}_a^\dagger(\mathbf{x}) \hat{\psi}_a(\mathbf{x}) \hat{\psi}_m(\mathbf{x})\end{aligned}\quad (1.41)$$

Here $\nu = \delta\mu\delta B$ is the energy detuning, $\delta\mu$ is the difference between magnetic moments of two free atoms and a bare molecule, and $\delta B = B - B_c$ is the magnetic field detuning where B_c is the magnetic field at resonance. The atom-molecule coupling strength is $g = \hbar\sqrt{2\pi a_{\text{bg}}\delta\mu\Delta B/m}$ where a_{bg} is the background scattering length, ΔB is the resonance width and m is the atomic mass. The T-matrices are $T_{\text{bg}} = 8\pi\hbar^2 a_{\text{bg}}/m$, $T_{\text{am}} = 6\pi\hbar^2 a_{\text{am}}/m$ and $T_{\text{mm}} = 4\pi\hbar^2 a_{\text{mm}}/m$, where a_{am} and a_{mm} are the atom-molecule and molecule-molecule scattering lengths, respectively.

This Hamiltonian can be rewritten as

$$\begin{aligned}\hat{H} = & \epsilon_m \hat{\psi}_m^\dagger \hat{\psi}_m + \epsilon_a \hat{\psi}_a^\dagger \hat{\psi}_a + g' \left(\hat{\psi}_m^\dagger \hat{\psi}_a^2 + \hat{\psi}_a^\dagger \hat{\psi}_m \right) + T'_{\text{bg}} \hat{\psi}_a^\dagger \hat{\psi}_a^\dagger \hat{\psi}_a \hat{\psi}_a \\ & + T'_{\text{mm}} \hat{\psi}_m^\dagger \hat{\psi}_m^\dagger \hat{\psi}_m \hat{\psi}_m + T'_{\text{am}} \hat{\psi}_m^\dagger \hat{\psi}_a^\dagger \hat{\psi}_a \hat{\psi}_m\end{aligned}\quad (1.42)$$

where $\epsilon_m = \hbar\omega_z/2 + \delta B$, $\epsilon_a = \hbar\omega_z/2$, $g' = \frac{g}{(2\pi)^{1/4}\sqrt{Al_z}}$, $T'_{\text{bg}} = \frac{T_{\text{bg}}}{2\sqrt{2\pi}Al_z}$, $T'_{\text{mm}} = \frac{T_{\text{mm}}}{2\sqrt{\pi}Al_z}$ and $T'_{\text{am}} = \frac{\sqrt{2}T_{\text{am}}}{\sqrt{3\pi}Al_z}$ where ω_z is the harmonic trap frequency along the z -direction, $l_z = \sqrt{\hbar/m\omega_z}$ is the harmonic oscillator length, and A is the area of the sample [23]. The equations of motion for the atomic and molecular annihilation operators derived by Zhang [23] are

$$\frac{d\hat{\psi}_a}{dt} = -i \left(\epsilon_a \hat{\psi}_a + 2g' \hat{\psi}_m \hat{\psi}_a^\dagger + 2T'_{\text{bg}} \hat{\psi}_a^\dagger \hat{\psi}_a^2 + T'_{\text{am}} \hat{\psi}_m^\dagger \hat{\psi}_m \hat{\psi}_a \right), \quad (1.43)$$

$$\frac{d\hat{\psi}_m}{dt} = -i \left(\epsilon_m \hat{\psi}_m + g' \hat{\psi}_a^2 + 2T'_{\text{mm}} \hat{\psi}_m^\dagger \hat{\psi}_m^2 + T'_{\text{am}} \hat{\psi}_m \hat{\psi}_a^\dagger \hat{\psi}_a \right). \quad (1.44)$$

In addition, the equations of motion for $\hat{M} = \hat{\psi}_m^\dagger \hat{\psi}_m$ are

$$\frac{d\hat{M}}{dt} = -\frac{1}{2} \frac{d\hat{N}}{dt} = ig' \left(\hat{\psi}_a^\dagger \hat{\psi}_m - \hat{\psi}_m^\dagger \hat{\psi}_a \right), \quad (1.45)$$

where $\hat{N}_t = \hat{N} + 2\hat{M}$ is a conserved quantity. Replacing the field operators with complex amplitudes, $\hat{\psi}_a \rightarrow \sqrt{N}e^{i\varphi_a}$ and $\hat{\psi}_m \rightarrow \sqrt{M}e^{i\varphi_m}$, gives us

$$\frac{d\varphi_a}{dt} = -\epsilon_a - 2g'\sqrt{M}e^{-i\varphi_R} - 2T'_{bg}N - T'_{am}M - 2ig'\sqrt{M}\sin\varphi_R, \quad (1.46)$$

$$\frac{d\varphi_m}{dt} = -\epsilon_m - g'\frac{N}{\sqrt{M}}e^{i\varphi_R} - 2T'_{mm}M - T'_{am}N + ig'\frac{N}{\sqrt{M}}\sin\varphi_R, \quad (1.47)$$

$$\frac{dM}{dt} = -\frac{1}{2} \frac{dN}{dt} = 2g'N\sqrt{M}\sin\varphi_R. \quad (1.48)$$

Therefore, the equations of motion for φ_R and M are

$$\frac{d\varphi_R}{dt} = g'\frac{N_t - 6M}{\sqrt{M}}\cos\varphi_R + 2\left(T'_{mm} - 2T'_{am} + 4T'_{bg}\right)M + \left(T'_{am} - 4T'_{bg}\right)N_t + \delta B - \frac{\hbar\omega_z}{2}, \quad (1.49)$$

$$\frac{dM}{dt} = 2g'(N_t - 2M)\sqrt{M}\sin\varphi_R. \quad (1.50)$$

Eq. (1.50) is identical to Eq. (1.19), whereas Eq. (1.49) evolves differently because of the extra term $2\left(T'_{mm} - 2T'_{am} + 4T'_{bg}\right)M$ which is absent in Eq. (1.20), as well as the additional offset.

In summary, reactions in the classical regime are governed by temperature-dependent rate constants and density-dependent collision rates. On the other hand, reaction rates scale with particle number in the quantum degenerate regime, where the wave-like nature of particles dominate, due to collective enhancement, while the direction of the reaction is determined by the phase difference φ_R . The molecular population increases for $\varphi_R = \pi/2 \pmod{2\pi}$, while it decreases for $\varphi_R = -\pi/2 \pmod{2\pi}$. Furthermore, in the quantum degenerate regime, the atomic and molecular populations can oscillate around the equilibrium point when $\varphi_R \approx 0$, whereas their classical counterparts relax monotonically to equilibrium without exhibiting any subsequent oscillations. These results demonstrate that phase plays a central role in reactions between coherent matter-wave fields – a hallmark of nonlinear wave-mixing dynamics – where the relative phase between reactants and products controls both the strength and the direction of the conversion process.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 System calibration

In this chapter, we present a brief overview of the experiment. As much of the technical details are well documented in previous theses, we focus more on the essential points relevant to the present work instead.

2.1.1 Magnetic field calibration

Magnetic Feshbach resonances play an important role in our work. Hence our experiments require precise knowledge of the resonance position. Microwave spectroscopy is a powerful tool for calibrating the magnetic field.

In our cooling procedure, Raman sideband cooling (RSC) pumps all ^{133}Cs atoms into the lowest hyperfine ground state, $|F = 3, m_F = 3\rangle$, where F and m_F are the quantum numbers for the total angular momentum and its projection along the direction of the magnetic field, respectively. Once all atoms occupy the lowest ground state, we turn on the microwave pulse to excite them to $|F = 4, m_F = 4\rangle$. Inelastic collisions between these two states causes atom loss. This loss effect is most pronounced when the microwave transition is driven on resonance.

To determine the magnetic field from the resonant microwave frequency, we apply the Breit–Rabi formula to the hyperfine energy levels of the $6^2\text{S}_{1/2}$ ground state. The Breit-Rabi formula is given by

$$E = -\frac{\Delta E_{hfs}}{2(2I + 1)} + g_I \mu_B m_F B \pm 0.5 \Delta E_{hfs} \left(1 + \frac{4m_F \xi}{2I + 1} + \xi^2 \right)^{1/2}, \quad (2.1)$$

where we used $\Delta E_{hfs} = 9.1926 \text{ GHz}$, Bohr magneton $\mu_B = h \times 1.3996 \text{ MHz/G}$, fine structure

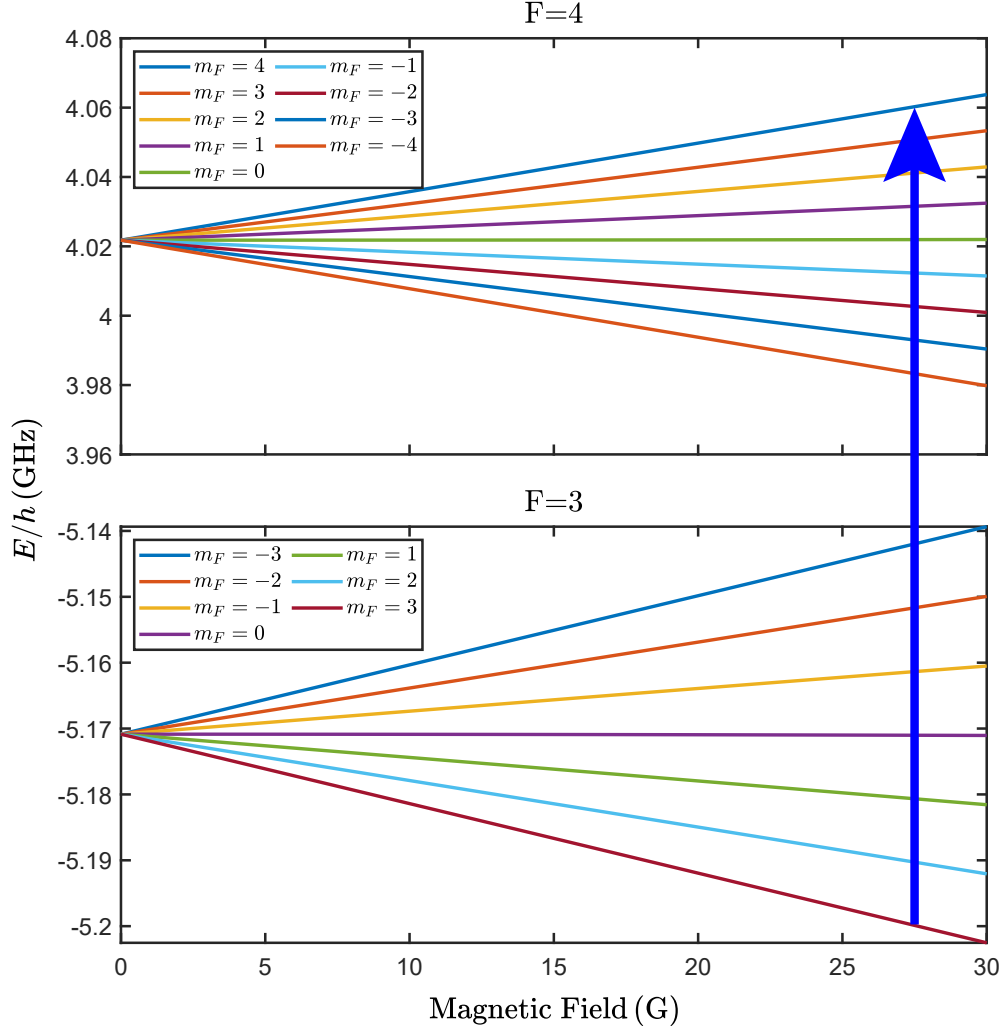


Figure 2.1: **Hyperfine Zeeman splitting of the cesium ground state manifold in the presence of an external magnetic field.** The upper manifold corresponds to the $F = 4$ hyperfine state while the lower manifold corresponds to the $F = 3$ state. The blue arrow indicates the microwave transition from $|F = 3, m_F = 3\rangle$ to $|F = 4, m_F = 4\rangle$. $|F = 3, m_F = 3\rangle$ is a strong field-seeking state while $|F = 4, m_F = 4\rangle$ is a weak field-seeking state. Most of our experiments take place around 20 G.

Lande g-factor $g_J = 2.0025$, nuclear g-factor $g_I = -0.0004$, nuclear spin $I = 7/2$, and $\xi = \frac{(g_J - g_I)\mu_B B}{\Delta E_{\text{hfs}}}$ [24, 25]. Here, ΔE_{hfs} is the hyperfine splitting between the $F = 4$ and $F = 3$ levels. This formula allows us to determine the magnetic field based on the resonant microwave frequency.

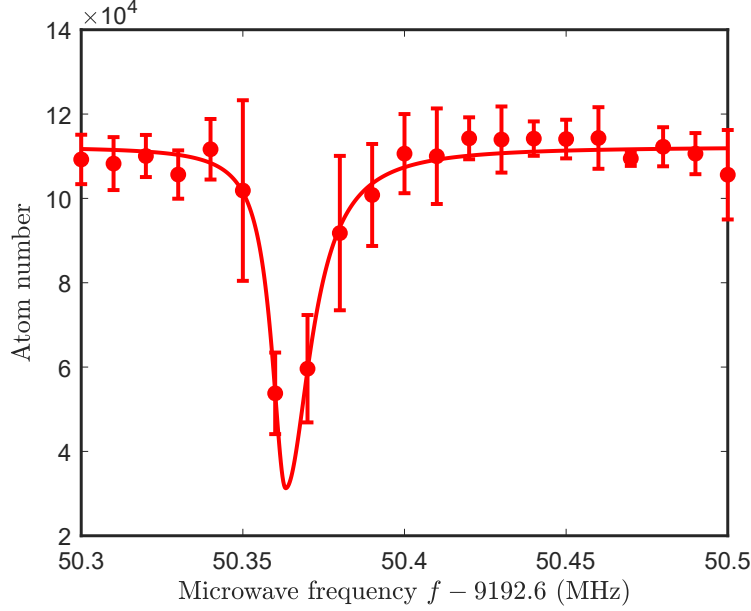


Figure 2.2: **Microwave spectroscopy.** Atoms are prepared in the $|F = 3, m_F = 3\rangle$ hyperfine state. A microwave pulse excites particles from $|F = 3, m_F = 3\rangle$ to $|F = 4, m_F = 4\rangle$. Inelastic collisions between these two states cause atom loss. In this dataset, a signal dip is located at approximately $f - 9192.6 = 50.365$ MHz, corresponding to 20.52 G.

2.1.2 Single pancake loading

We start with 1.2×10^5 Bose-condensed ^{133}Cs atoms in a crossed dipole trap at magnetic field $B \approx 20.4$ G. The Bose-Einstein condensate (BEC) has a temperature of approximately 10 nK and a condensate fraction close to 90%. Once evaporative cooling ends, the BEC is loaded into a two-dimensional (2D) cylindrical flat-bottomed trap. The atoms are trapped by a blue-detuned ring-like barrier generated by a digital micromirror device (DMD) in the radial direction while vertical confinement is provided by two intersecting red-detuned dipole trap beams. These two beams interfere to create a one-dimensional (1D) optical lattice along the vertical axis. The vertical lattice axial frequency is set to $\omega_z = 2\pi \times 590$ Hz.

In our experiment, we load the BEC into a single vertical lattice site, which has much tighter vertical confinement than the crossed dipole trap. The vertical lattice has a lattice spacing of approximately $4 \mu\text{m}$ while the initial BEC has a thickness of around $30 \mu\text{m}$. To load the BEC into a single site, we first adjust the magnetic field gradient and then

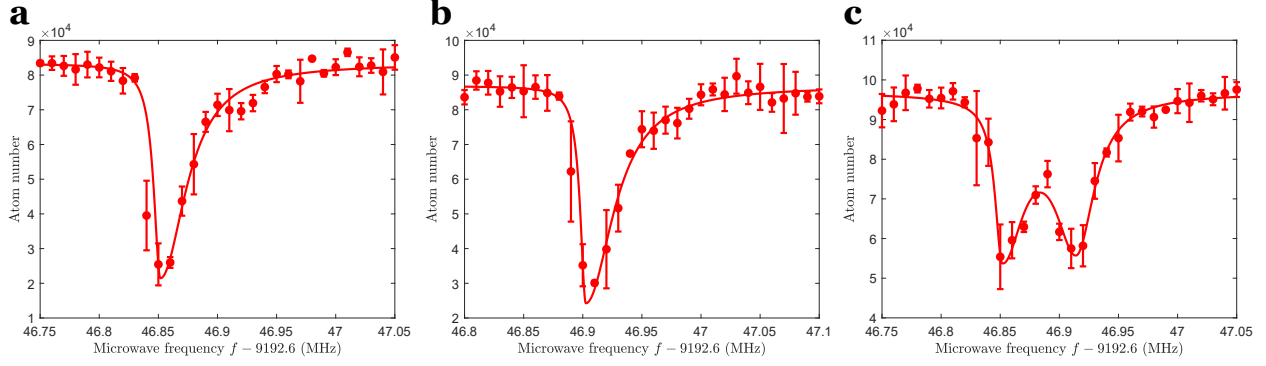


Figure 2.3: **Single pancake check.** **a**, Atoms are loaded into a single site resonant to $f - 9192.6 = 46.85$ MHz, corresponding to $B = 19.09$ G. **b**, Atoms are loaded into a single site resonant to $f - 9192.6 = 46.90$ MHz, corresponding to $B = 19.11$ G. **c**, Atoms are loaded into two sites at 46.85 MHz and 46.91 MHz. The two sites are separated by approximately 60 kHz, qualitatively consistent with our expectations.

adiabatically ramp up the vertical lattice potential so that the gradient pushes the atoms into the desired site.

To detect single site loading, we increase the magnetic field gradient and perform microwave spectroscopy on the atoms. When the final gradient is set to $B' = 50$ G/cm, the field difference ΔB across adjacent lattice sites is equivalent to $\Delta B = 20$ mG. Since the Zeeman energy levels split linearly at weak magnetic fields, $E_{|F, m_F\rangle} = g_F \mu_B m_F B$, the energy difference between the two sites is $\Delta E = E_{|4,4\rangle} - E_{|3,3\rangle} = \frac{7}{4} \cdot h \cdot 1.4 \text{ (MHz/G)} \cdot \Delta B = h \times 49$ kHz. This calculation shows that the magnetic field variation between neighboring lattice sites produces a small shift in the resonant microwave frequency which can be detected by microwave spectroscopy. Therefore, we detect atom loss at two distinct frequencies separated by ≈ 49 kHz, as shown Fig. 2.3. To summarize, microwave spectroscopy can also be used as a diagnostic to confirm single site loading in the vertical lattice in the presence of a strong magnetic field gradient.

2.1.3 Characterization of the modulation transfer function

When loading the BEC into a single vertical lattice site, we must also consider which site yields the highest imaging resolution. Due to the finite resolution of our imaging system, the real atomic density distribution $n(\mathbf{r})$ is blurred by the point spread function $P(\mathbf{r})$. Therefore, the measured atomic density distribution $n_{\text{exp}}(\mathbf{r})$ becomes

$$n_{\text{exp}}(\mathbf{r}) = \int d\mathbf{r}' n(\mathbf{r}') P(\mathbf{r} - \mathbf{r}'). \quad (2.2)$$

When the point spread function is a delta function, the measured density distribution is equivalent to the true density distribution. In Fourier space, Eq. (2.2) can be approximated as

$$\delta n_{\text{exp}}(\mathbf{k}) \approx \delta n(\mathbf{k}) P(\mathbf{k}), \quad (2.3)$$

where $\delta n_{\text{exp}}(\mathbf{k})$ is the discrete Fourier transform. Here, we used $\delta n(-\mathbf{k}) = \delta n^*(\mathbf{k})$ since $\delta n(\mathbf{r})$ is real. The k -space density fluctuation $\delta n(\mathbf{k})$ is related to the static structure factor $S(\mathbf{k})$ via

$$S(\mathbf{k}) = \frac{\langle \delta n(\mathbf{k}) \delta n(-\mathbf{k}) \rangle}{N} = \frac{\langle |\delta n(\mathbf{k})|^2 \rangle}{N}, \quad (2.4)$$

where N is the total particle number [26]. Substituting Eq. (2.4) into Eq. (2.3), we obtain

$$\langle |\delta n_{\text{exp}}(\mathbf{k})|^2 \rangle \approx N S(\mathbf{k}) \mathcal{M}^2(\mathbf{k}), \quad (2.5)$$

where the modulation transfer function $\mathcal{M}(\mathbf{k}) = |P(\mathbf{k})|$ is the magnitude of the point spread function in Fourier space. The modulation transfer function (MTF) characterizes the imaging system's response to a given spatial frequency $\mathbf{k}$. For a thermal gas with low phase-space density, the structure factor can be approximated as $S(\mathbf{k}) \approx 1$, for wavevectors up to the inverse of the thermal de-Broglie wavelength $k \lesssim \lambda_{\text{dB}}^{-1}$.

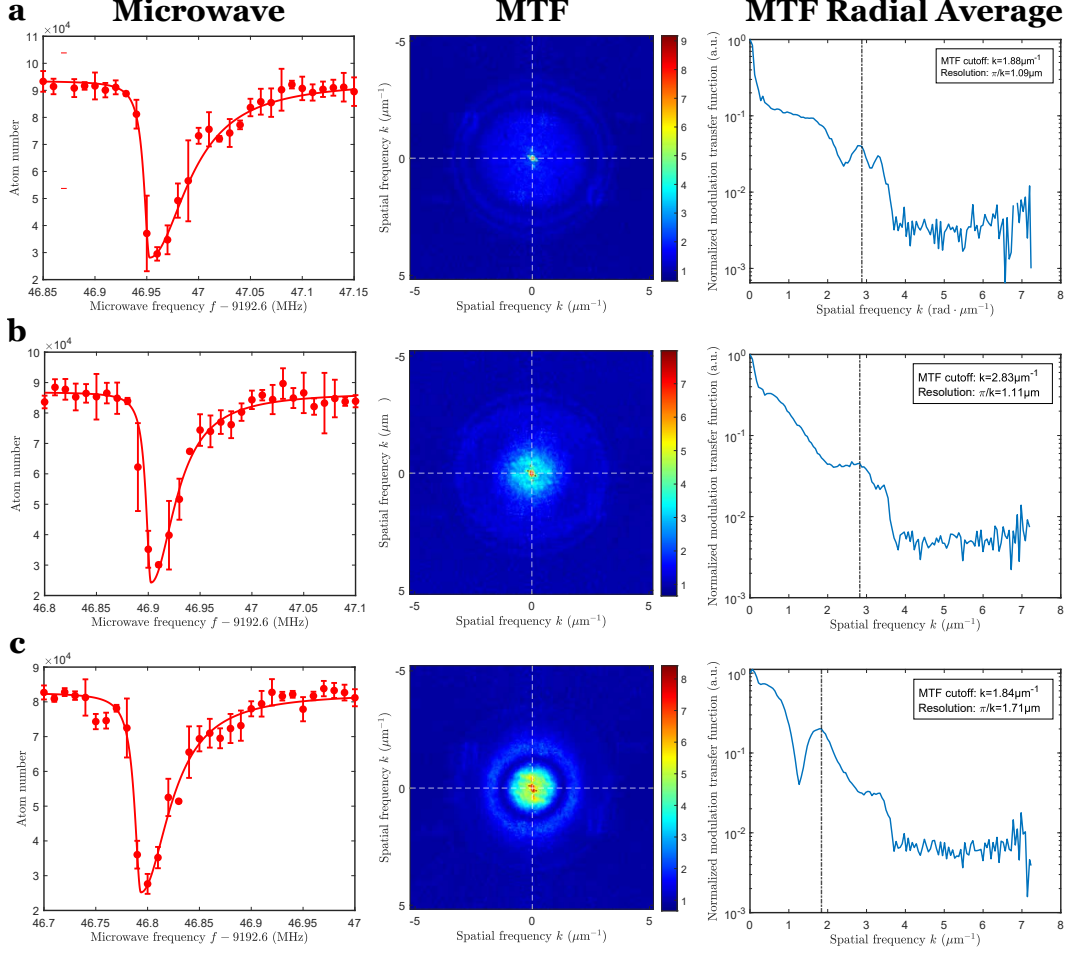


Figure 2.4: **Characterization of the modulation transfer function extracted from the density-fluctuation power spectrum.** The MTF is measured from atoms loaded into different vertical lattice sites. The hard edge or plateau corresponds to finite range of imaging response system. **a**, Atoms are loaded into a single site resonant to 46.95 MHz. The MTF cutoff frequency is set to $k = 2.88 \mu\text{m}^{-1}$, corresponding to a spatial resolution of $1.09 \mu\text{m}$. **b**, Atoms are loaded into an adjacent site, one site below the first one, and resonant to 46.9 MHz. The MTF cutoff frequency is set to $k = 2.83 \mu\text{m}^{-1}$, corresponding to a spatial resolution of $1.11 \mu\text{m}$. **c**, Atoms are loaded into a site, three sites below the first one, and resonant to 46.8 MHz. The MTF cutoff frequency is set to $k = 1.84 \mu\text{m}^{-1}$, corresponding to a spatial resolution of $1.71 \mu\text{m}$.

Therefore, the power spectrum of density fluctuations in a thermal gas is given by

$$\langle |\delta n_{\text{exp}}(\mathbf{k})|^2 \rangle \approx N \mathcal{M}^2(\mathbf{k}). \quad (2.6)$$

To extract the imaging system's MTF $\mathcal{M}$, we first quench the magnetic field to the Feshbach

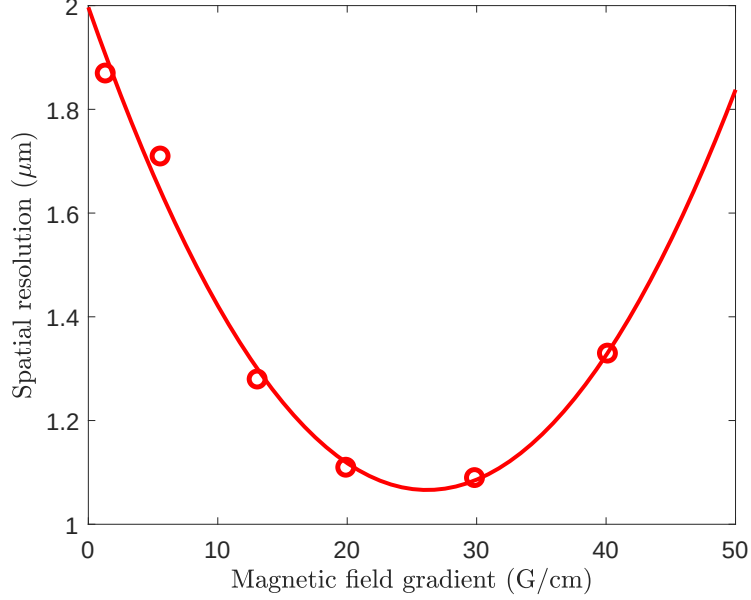


Figure 2.5: **Comparison of imaging resolution at different vertical lattice sites.** The imaging resolution reaches a minimum of $1.07 \mu\text{m}$ at $B' \approx 30 \text{ G/cm}$. Here each data point corresponds to an individual lattice site.

resonance to heat up the BEC and measure its density fluctuation power spectrum, see Fig. 2.4. Here, we load atoms into different vertical lattice sites by adjusting the magnetic field gradient and compare their normalized MTFs. In a perfect, aberration-free imaging system, the MTF decreases smoothly and monotonically from unity at low spatial frequencies to zero at the diffraction-limited cutoff frequency. In our measurements, the MTF decreases with increasing spatial frequency until it reaches a hard edge or plateau. This hard edge corresponds to the maximum spatial frequency transmitted by the imaging system and marks its theoretical resolution limit. Thus we define this edge as the diffraction-limited cutoff frequency, from which we determine the corresponding real-space resolution.

In Fig. 2.5, we compare the imaging resolution at different vertical lattice sites. By tuning the magnetic field gradient, we load the atoms into the optimal site and achieve a resolution as small as $1.07 \mu\text{m}$ without moving the microscope objective. However, this method is only effective when the focal plane of the microscope objective has not been significantly displaced from the original position of the BEC; otherwise, the objective must be adjusted.

2.2 Preparation of molecular BEC

A magnetic Feshbach resonance occurs when a weakly bound molecular state is magnetically tuned to have the same energy as two free atoms, causing strong coupling between the scattering state and the molecular state [27]. Colliding atoms are prepared in an entrance channel, while the molecular state at energy E_c resides in a closed channel that is energetically inaccessible at long range. The asymptotic limit of the entrance channel matches the threshold of the atomic continuum. Near a Feshbach resonance, the energy of the molecular state can be modeled as a linear Zeeman shift, $E_c = \delta\mu(B - B_c)$, where $\delta\mu$ is the relative magnetic moment of the two channels and B_c is the magnetic field at resonance.

Our experiment starts with a pure BEC of 1.2×10^5 cesium atoms with a temperature of 11(2) nK prepared in a two-dimensional disk-shaped, flat-bottomed trap with a radius of 21 μm . The atoms are loaded into a 1D vertical lattice with trap frequency of $\omega_z = 2\pi \times 590$ Hz that provides strong vertical confinement. The condensate is prepared at a magnetic field of $B = 20.4$ G with an atomic scattering length $a = 180a_0$, where a_0 is the Bohr radius and the chemical potential is $\mu = k_B \times 40$ nK [15].

To create molecules, we rapidly sweep the magnetic field across the narrow g -wave Feshbach resonance at 19.849 G with a width of 8.3 mG in 1.5 ms to couple the Cs atoms into Cs_2 molecules in $|f = 4, m_f = 4; l = 4, m_l = 2\rangle$ where f is the total angular momentum quantum number of the molecule, l is the molecular orbital angular momentum quantum number, and m_f and m_l are the projections of f and l along the direction of the magnetic field, respectively [15, 28]. These molecules are spin-polarized and occupy a single high lying rovibrational state. During the ramp, the reaction occurs when the magnetic field is on resonance and terminates as the field moves away. The ramp converts the atomic BEC into a molecular BEC of up to 2×10^4 molecules with a temperature of 10(3) nK [15]. The ramp is followed by a fast quench of the field to 17.2 G and then a resonant beam to remove any remaining atoms. To detect molecules, we dissociate them into atoms by ramping the

magnetic field above the resonance and perform absorption imaging on the atoms.

2.3 Optical lattices

In this work, we use optical lattices to imprint arbitrary phases on the sample. Optical lattices are standing waves of light that act as periodic potentials for atoms and molecules. In this section, we characterize their response to such potentials.

2.3.1 Experimental setup

The optical lattice beams are generated by a Nd:YAG laser with wavelength $\lambda = 1064$ nm. After passing through the atomic sample, the incident dipole trap beam is sent through a pair of acousto-optic modulators (AOMs) and then retro-reflected to propagate along the same beam path back to the main vacuum chamber. This pair of AOMs is used to tune the frequency of the retro-reflected beam. When the incident beam overlaps with the retro-reflected beam, they interfere to create an optical standing wave.

To represent the two counter-propagating beams that form a standing wave, we write the total electric field to $\tilde{E} = \tilde{E}_1 + \tilde{E}_2 = E_1 e^{i(k_L z - \omega_1 t)} + E_2 e^{-i(k_L z + \omega_2 t)}$, where E_1 and E_2 are the electric field amplitudes, and ω_1 and ω_2 are the optical frequencies of the incident and retro-reflected beams, respectively. Here $k_L = 2\pi/\lambda$ is the lattice wavenumber. The squared magnitude of the total electric field is

$$|\tilde{E}(z, t)|^2 = (E_1 + E_2)^2 - 4E_1 E_2 \sin^2 \left(k_L z - \frac{\delta\omega t}{2} \right), \quad (2.7)$$

where $\delta\omega = \omega_1 - \omega_2$. Since the time-averaged intensity of a monochromatic field is given as $I = \frac{1}{2}c\epsilon_0|\tilde{E}|^2$, where c is the speed of light and ϵ_0 is the permittivity of free space, substituting the laser intensities $I_1 = \frac{1}{2}c\epsilon_0|\tilde{E}_1|^2$ and $I_2 = \frac{1}{2}c\epsilon_0|\tilde{E}_2|^2$ into Eq. (2.7) yields

$$\begin{aligned}
|\tilde{E}(z, t)|^2 &= \left(\sqrt{\frac{2I_1}{c\epsilon_0}} + \sqrt{\frac{2I_2}{c\epsilon_0}} \right)^2 - 4\sqrt{\frac{2I_1}{c\epsilon_0}}\sqrt{\frac{2I_2}{c\epsilon_0}} \sin^2 \left(k_L z - \frac{\delta\omega t}{2} \right) \\
&= \frac{2}{c\epsilon_0} \left[\left(\sqrt{I_1} + \sqrt{I_2} \right)^2 - 4\sqrt{I_1 I_2} \sin^2 \left(k_L z - \frac{\delta\omega t}{2} \right) \right].
\end{aligned} \tag{2.8}$$

The electric field induces a dipole moment in the particle, $\tilde{p} = \alpha \tilde{E}$. Since the interaction potential experienced by a particle with an induced dipole moment is given by

$$U_{\text{dip}} = -\frac{1}{2} \langle \tilde{p} \tilde{E} \rangle = -\frac{\alpha}{2} \langle \tilde{E}^2 \rangle = -\frac{\alpha}{2} \Re(\tilde{E} \tilde{E}^*) = -\frac{1}{4} \alpha |\tilde{E}|^2, \tag{2.9}$$

where α is the frequency-dependent electric dipole polarizability, we substitute Eq. (2.8) into Eq. (2.9) to obtain

$$U_{\text{dip}} = -\frac{1}{4} \alpha |\tilde{E}|^2 = -\frac{\alpha}{2c\epsilon_0} \left[\left(\sqrt{I_1} + \sqrt{I_2} \right)^2 - 4\sqrt{I_1 I_2} \sin^2 \left(k_L z - \frac{\delta\omega t}{2} \right) \right], \tag{2.10}$$

In Eq. (2.10), the first term provides a slowly varying weak trapping potential, while the second term generates a standing-wave fringe pattern that forms the 1D optical lattice. Hence, the lattice is stationary for $\delta\omega = 0$, whereas a nonzero $\delta\omega$ causes the lattice to move. For $\delta\omega \neq 0$, the lattice moves with velocity $\frac{\delta\omega}{2k_L}$. We determine the polarizability $\frac{\alpha}{2c\epsilon_0}$ for both Cs atoms and Cs₂ molecules later on in this chapter.

2.3.2 Kapitza-Dirac and Bragg diffraction

We perform matter-wave diffraction on the atomic and molecular BECs to verify their spatial coherence. Kapitza-Dirac diffraction is realized by turning on a static lattice for a short duration, which scatters particles symmetrically into multiple momentum modes $k = \pm 2k_L, \pm 4k_L, \dots$ [29], see Figs. 2.7a, b.

On the other hand, Bragg diffraction resonantly couples particles from the ground state to the $2k_L$ momentum state using a moving lattice [30], see Figs. 2.7c, d. The retro-reflected

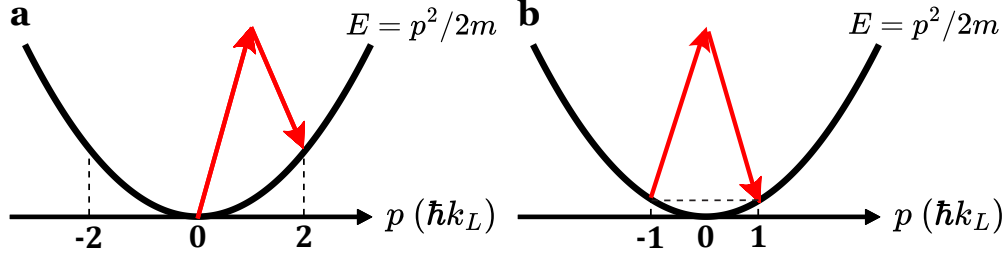


Figure 2.6: **Two-photon Bragg transition in the lattice co-moving frame** **a**, Lab frame, and **b**, lattice co-moving frame, where the $-\hbar k_L$ and $+\hbar k_L$ momentum states become degenerate.

beam is detuned by $\Delta f = 5.304$ kHz for atoms and $\Delta f = 2.652$ kHz for molecules. By setting the AOMs to $+80$ MHz $+\Delta f/2$ and -80 MHz, the retro-reflected beam passes through the AOMs twice and thus acquires the desired detuning Δf . The frequency detunings correspond to the energy difference between $k = 0$ and $2k_L$ momentum states. For molecules, its kinetic energy is reduced by a factor of two because its mass is two times that of atoms. Here Bragg diffraction occurs because the lattice resonantly couples two momentum states that become degenerate in the lattice co-moving frame.

To measure the atomic and molecular populations in different momentum modes, we perform a 2D time-of-flight (TOF) expansion to spatially separate atoms and molecules in different orders. We expand the sample in the radial $x-y$ direction by shutting off the DMD potential barrier while keeping the vertical lattice turned on in the z -direction such that the sample only expands in the radial plane. Before applying the lattice pulse, the scattering length is quenched to $0a_0$ for atoms, while it is fixed at $220a_0$ for molecules [15].

After $t_{\text{TOF}} = 15$ ms, when the diffracted orders are sufficiently separated, we image the sample and determine their populations by counting the particle number in each momentum mode. The TOF is short enough such that the diffracted components retain the disk-like shape of the initial BEC. To obtain precise particle numbers, we subtract the background signal and integrate the particle number density within the circular area of the BEC for each diffracted momentum mode.

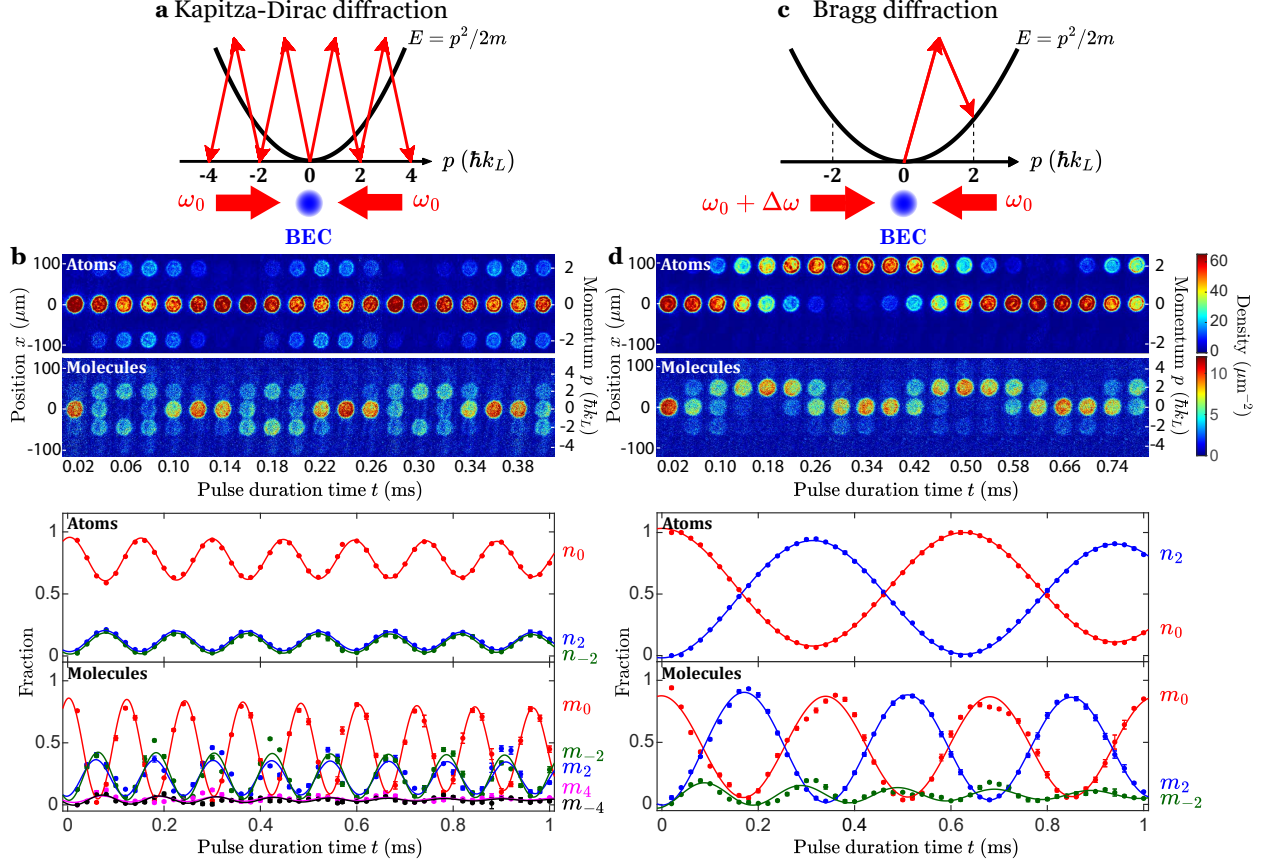


Figure 2.7: Kapitza-Dirac and Bragg diffraction of atomic and molecular BECs. **a**, Kapitza-Dirac diffraction is induced by a pulse of counter-propagating laser beams with identical frequencies ω_0 (wavelength $\lambda = 1064$ nm) for a duration of time t . The optical lattice potential diffracts particles at zero momentum $k = 0$ to $\pm 2k_L$, $\pm 4k_L$..., where $k_L = 2\pi/\lambda$ is the lattice momentum. **b**, Rabi oscillations of the atoms and molecules in the momentum space for Kapitza-Dirac diffraction. Images are taken after a 15 ms time-of-flight. Here n_j and m_j denote the population fractions of atoms and molecules with momentum jk_L , respectively. The solid lines are sinusoidal fits which yield the Rabi frequencies $2\pi \times 6.77(1)$ kHz for atoms and $2\pi \times 8.31(1)$ kHz for molecules with momentum $k = 0$ and $\pm 2k_L$. **c**, Bragg diffraction is realized by detuning one of the lattice beams by $\Delta\omega = 4E_R/\hbar = 2\pi \times 5.304$ kHz for atoms and $2E_R/\hbar = 2\pi \times 2.652$ kHz for molecules. The pulse resonantly scatters particles to momentum $k = 2k_L$. Here, $E_R = \hbar^2 k_L^2 / 2m$ is the atomic recoil energy and m is the atomic mass. **d**, Rabi oscillations of the atoms and molecules for Bragg diffraction. The solid lines are sinusoidal fits which yield the Rabi frequency $2\pi \times 1.59(1)$ kHz for atoms and $2\pi \times 2.95(1)$ kHz for molecules. Decoherence rates of the observed oscillations are lower than 0.2 ms^{-1} . Off-resonant excitations to momentum $k = -2k_L$ are stronger for molecules compared to atoms due to the larger Rabi coupling and smaller detuning [?]. Images shown here are averaged over five independent measurements. Error bars show $1\text{-}\sigma$ standard deviations of the means.

Both diffraction processes induce coherent oscillations of atomic and molecular populations between zero and finite momentum modes. We use an empirical function to fit the atomic and molecular Rabi oscillations in Fig. 2.7

$$P(t) = P(0) \cos(\Omega t + \theta) e^{-\eta t} + C, \quad (2.11)$$

where P is the population, θ is the phase shift, η is the decoherence rate and C is a constant. The fitting results are listed in Tables 2.1 and 2.2. From these measurement results, we determine the lattice potential depth as $4.70(2) E_R$ for atoms and $9.31(2) E_R$ for molecules, for Kapitza-Dirac diffraction in Fig. 2.7b, and $2.41(1) E_R$ for atoms and $4.83(1) E_R$ for molecules, for Bragg diffraction in Fig. 2.7d. Here m denotes the cesium mass and E_R denotes the recoil energy, $E_R = \hbar^2 k_L^2 / 2m$, which is defined as the kinetic energy acquired by an atom when it absorbs or emits a photon with wavenumber k_L . The recoil energy sets the natural energy scale for optical lattices. Since the lattice beam intensity is constant for both atoms and molecules, the difference in their potential depths suggests their dynamical polarizabilities are also different, a point we address in a later section.

From the coherent oscillations between different momentum states, we estimate the coherence length as $l_c = v_{\text{rel}} \tau_c$, where $v_{\text{rel}} = 2\pi\hbar/\lambda m$ is the relative velocity of the excited mode and $\tau_c = 1/\eta$ is the coherence time. From the Bragg-diffraction measurements, we obtain a decoherence rate of $\eta_a = 0.10\text{ms}^{-1}$ for atoms and $\eta_m = 0.15\text{ms}^{-1}$ for molecules. These values yield a coherence length of $l_c \approx 56 \mu\text{m}$ for atoms and $l_c \approx 20 \mu\text{m}$ for molecules, both of which are comparable to the size of our sample.

Table 2.1: **Oscillation frequencies and decoherence rates of the Kapitza-Dirac diffracted atomic and molecular populations.** Obtained from the fits in Fig. 2.7b.

Atoms			Molecules		
Momentum	Frequency	Decoherence rate	Momentum	Frequency	Deoherence rate
k	$\Omega/2\pi$ (kHz)	η (ms ⁻¹)	k	$\Omega/2\pi$ (kHz)	η (ms ⁻¹)
0	6.77(1)	0.23(1)	0	8.31(1)	0.22(2)
$-2k_L$	6.76(1)	0.19(1)	$-2k_L$	8.30(3)	0.27(4)
$2k_L$	6.78(1)	0.22(2)	$2k_L$	8.35(2)	0.16(6)

Table 2.2: **Oscillation frequencies and decoherence rates of the Bragg diffracted atomic and molecular populations.** Obtained from the fits in Fig. 2.7d.

Atoms			Molecules		
Momentum	Frequency	Decoherence rate	Momentum	Frequency	Decoherence rate
k	$\Omega/2\pi$ (kHz)	η (ms ⁻¹)	k	$\Omega/2\pi$ (kHz)	η (ms ⁻¹)
0	1.60(1)	0.11(2)	0	2.93(2)	0.15(1)
$2k_L$	1.59(1)	0.10(1)	$2k_L$	2.95(1)	0.14(1)

2.3.3 Lattice potential depth calibration

To model how atoms respond to the 1D lattice potential, we start from the single particle Hamiltonian

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 \cos^2(k_L x), \quad (2.12)$$

where V_0 is the lattice potential depth. Here we define the lattice potential as $V_0 \cos^2(k_L x)$, rather than $V_0 \sin^2(k_L x)$ as in Eq. (2.10), for later convenience. The Schrödinger equation

can be solved using the trial solution, $\psi(x) = \sum_{n \in \mathbf{Z}} c_n(t) e^{iqx} e^{ink_L x}$, where $c_n(t)$ is the probability amplitude for the n^{th} mode and q is the initial momentum offset. Substituting this ansatz into the Schrödinger equation yields a system of coupled differential equations

$$i\hbar\dot{c}_n = \left(\frac{\hbar^2(q + nk_L)^2}{2m} + \frac{V_0}{2} \right) c_n + \frac{V_0}{4} (c_{n-2} + c_{n+2}), \quad (2.13)$$

showing that each n^{th} mode couples to its $(n \pm 2)^{\text{th}}$ neighbors [31]. Thus, the matrix Hamiltonian can be expressed in the tridiagonal form as

$$\begin{pmatrix} \ddots & & & & \\ & \ddots & & & \\ & & \frac{\hbar^2(q+2k_L)^2}{2m} + \frac{V_0}{2} & & \frac{V_0}{4} \\ & & \frac{V_0}{4} & \frac{\hbar^2 q^2}{2m} + \frac{V_0}{2} & \frac{V_0}{4} \\ & & & \frac{V_0}{4} & \frac{\hbar^2(q-2k_L)^2}{2m} + \frac{V_0}{2} & \ddots \\ & & & & \ddots & \ddots \end{pmatrix}.$$

For Kapitza-Dirac diffraction, we set q to zero and recover the kinetic energies corresponding to momenta $k = 0, \pm 2k_L, \pm 4k_L, \dots$, each shifted with an additional offset of $V_0/2$. The lattice coupling is given by the off-diagonal matrix element $V_0/4$.

To illustrate how Bragg diffraction emerges in this Hamiltonian, we derive the Bragg resonance condition. Subtracting the uniform offset $V_0/2$, we define the kinetic energies as $E_n = \hbar^2 k'^2 / 2m = \hbar^2 (q + nk_L)^2 / 2m$. In the moving frame, the kinetic energies become

$$E'_n = \frac{(\hbar(q + nk_L) - mv_L)^2}{2m}, \quad (2.14)$$

where v_L is the lattice velocity. Equating $E'_n = E'_{n+2}$ yields the resonance condition

$$mv_L = \hbar(q + (n+1)k_L). \quad (2.15)$$

Substituting $n = -2$ into the resonance condition gives us $mv_L = \hbar(q - k_L)$. By choosing $q = k_L$, the lattice velocity becomes $v_L = 0$, i.e., a stationary lattice. Thus, resonant coupling between $n = -2$ and $n = 0$ occurs only at $q = k_L$. To verify the degeneracy of these states, we substitute $q = k_L$ into the matrix Hamiltonian, giving us

$$\begin{pmatrix} \ddots & & \ddots & & & \\ & \ddots & \frac{9\hbar^2 k_L^2}{2m} + \frac{V_0}{2} & \frac{V_0}{4} & & \\ & & \frac{V_0}{4} & \frac{\hbar^2 k_L^2}{2m} + \frac{V_0}{2} & \frac{V_0}{4} & \\ & & & \frac{V_0}{4} & \frac{\hbar^2 k_L^2}{2m} + \frac{V_0}{2} & \ddots \\ & & & & \ddots & \ddots \end{pmatrix},$$

which shows that the momentum states $k' = q - 2k_L = -k_L$ and $q = k_L$ become degenerate.

Computing the time-dependent momentum state populations requires truncating the matrix Hamiltonian. However, this truncation becomes unreliable in the strong-coupling regime, where the omission of higher-order momentum components degrades accuracy. Hence, a different approach is required to fully characterize the response.

Here we examine Kapitza–Dirac and Bragg diffraction within the framework of lattice band structure. In the extended-zone representation, Kapitza–Dirac diffraction excites particles from the ground band to the 2nd excited band at quasimomentum $q = 0$ because only even-parity bands are accessible. Therefore, the Rabi oscillation frequency ω_{KD} in the Kapitza–Dirac regime is given by

$$\hbar\omega_{KD} = E_{n=2,q=0} - E_{n=0,q=0}, \quad (2.16)$$

where n denotes the band index. On the other hand, Bragg diffraction transfers particles in the ground band with momentum $-\hbar k_L$ to the first excited band with momentum $\hbar k_L$.

Therefore, the Rabi oscillation frequency ω_B in the Bragg regime is given by

$$\hbar\omega_B = E_{n=1,q=k_L} - E_{n=0,q=k_L}, \quad (2.17)$$

where we used $E_{n=0,q=-k_L} = E_{n=0,q=k_L}$. Rather than diagonalizing the truncated matrix Hamiltonian, we obtain the band eigenstates and eigenenergies by solving the Mathieu equation,

$$\frac{d^2y}{dz^2} + (\epsilon - 2\nu \cos 2z)y = 0, \quad (2.18)$$

which admits π -periodic solutions of even parity when $\epsilon = \epsilon_a(r, \nu)$ and odd parity when $\epsilon = \epsilon_b(r, \nu)$, where $\epsilon_a(r, \nu)$ and $\epsilon_b(r, \nu)$ are the even and odd Mathieu characteristic values. The parameter r is the characteristic exponent of the Mathieu equation and is related to the quasimomentum in our system by $r = q/k_L$. Mapping the Schrödinger equation onto the Mathieu equation yields the dimensionless atomic eigenenergies

$$E_{a,q} = \epsilon_a(q/k, \nu) + \frac{1}{2} \frac{V_0}{E_R} \quad (\text{even parity}), \quad (2.19)$$

$$E_{b,q} = \epsilon_b(q/k, \nu) + \frac{1}{2} \frac{V_0}{E_R} \quad (\text{odd parity}). \quad (2.20)$$

where $\nu = \frac{V_0}{4E_R}$. Substituting these solutions into Eq. (2.16) and (2.17) gives us

$$\hbar\omega_{KD} = E_{a,2k_L} - E_{a,0} = \epsilon_a(2, \nu) - \epsilon_a(0, \nu), \quad (2.21)$$

$$\hbar\omega_B = E_{b,k_L} - E_{a,k_L} = \epsilon_b(1, \nu) - \epsilon_a(1, \nu). \quad (2.22)$$

Thus, we can calibrate the lattice potential depth by comparing the measured Rabi oscillation frequencies to their theoretical values using Eqs. (2.21) and (2.22). The molecular eigenenergies are obtained in a similar manner by solving the Mathieu equation with some modifications. The resulting dimensionless molecular eigenenergies are given by

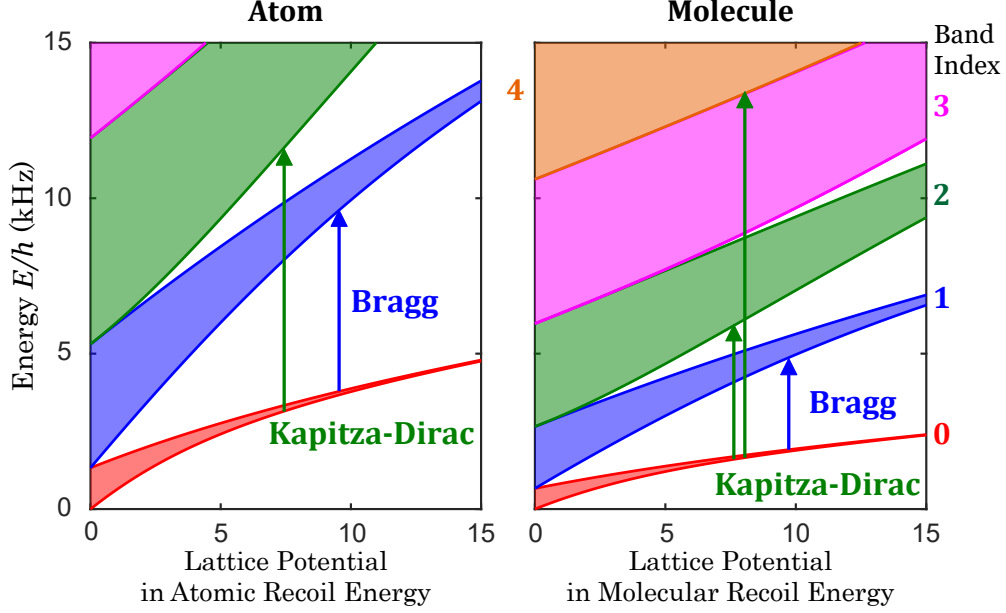


Figure 2.8: **Energy spectrum of Bloch bands as a function of lattice potential depth.** Band energies of atoms and molecules in a 1D lattice in units of atomic and molecular recoil energies, respectively. The energies are obtained from the solution of the Mathieu equation. Band index is indicated by different colors. The lower and upper edges of even-numbered bands correspond to band energies at quasimomentum $q = 0$ and $q = k_L$, respectively. On the other hand, the lower and upper edges of odd-numbered bands correspond to band energies at quasimomentum $q = k_L$ and $q = 0$, respectively. In Kapitza-Dirac diffraction, particles are excited from the lower edge of the ground band to the lower edge of the 2nd excited band. In Bragg diffraction, particles are excited from upper edge of the ground band to the lower edge of the 1st excited band. Here, the molecular recoil energy E_R^{mol} is half the atomic recoil energy E_R .

$$E'_{a,q} = \frac{1}{2} \left(\epsilon'_a(q/k, \nu') + \frac{V_0}{E_R} \right) \quad (\text{even parity}), \quad (2.23)$$

$$E'_{b,q} = \frac{1}{2} \left(\epsilon'_b(q/k, \nu') + \frac{V_0}{E_R} \right) \quad (\text{odd parity}), \quad (2.24)$$

where $\nu' = \frac{V_0}{2E_R}$. A full derivation of the dimensionless Mathieu equation for both atoms and molecules is provided in Appendix A. Using Eqs. (2.19) and (2.20), as well as (2.23) and (2.24), we plot the Bloch band energy spectrum as a function of the lattice potential depth, see Figs. 2.8 and 2.9. The larger molecular mass, $m_{\text{mol}} = 2m$, compresses the band structure, leading to narrower bands and smaller band gaps.

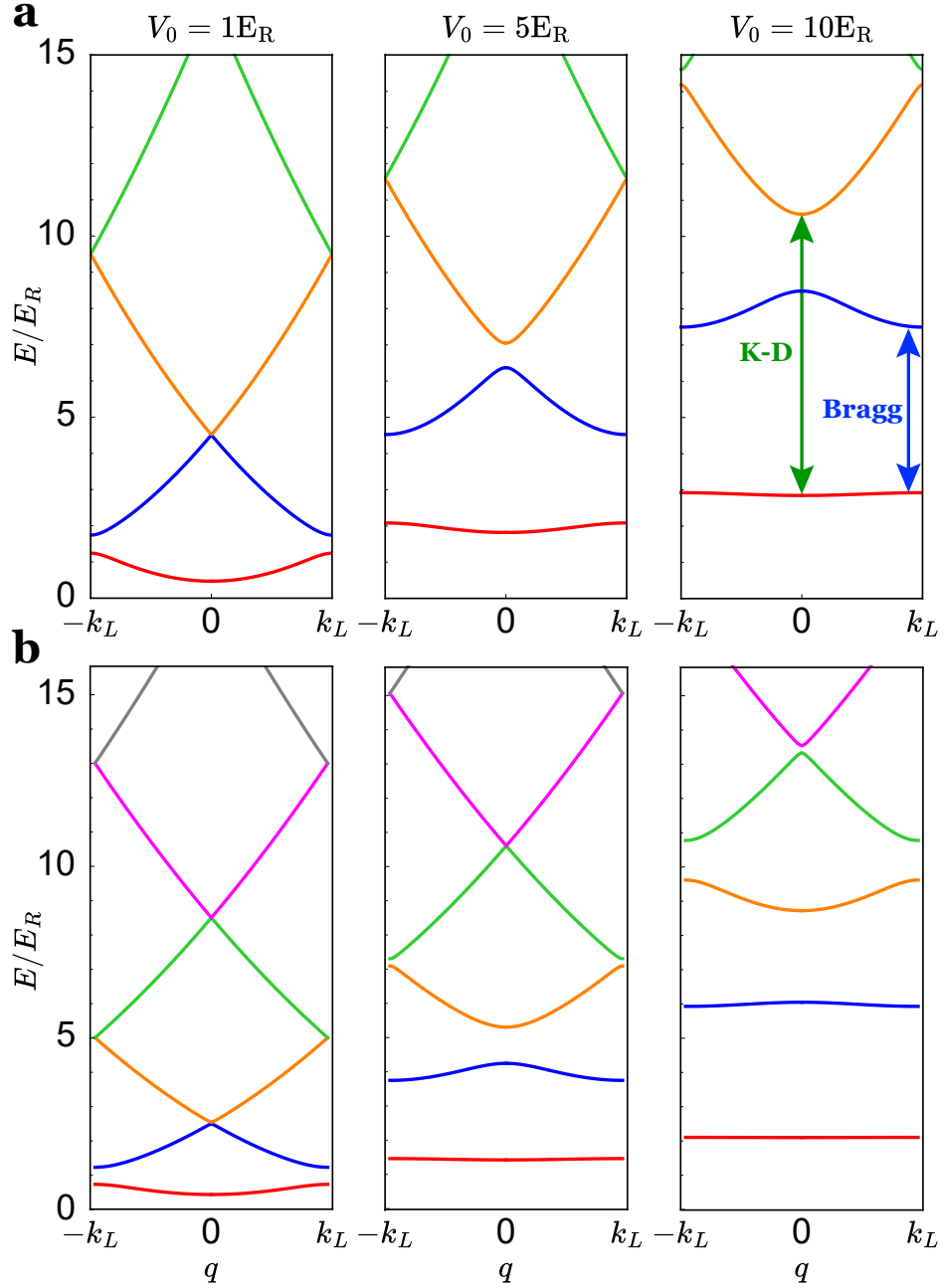


Figure 2.9: **1D band structure for atoms and molecules.** Band structure for **a**, atoms and **b**, diatomic molecules at different lattice potential depths (in units of atomic recoil energy E_R). The colors red, blue, orange, green, magenta, gray denote the 0th, 1st, 2nd, 3rd, 4th, 5th excited bands, respectively. Kapitza-Dirac diffraction (green double-headed arrow) excites particles from the ground band to the 2nd excited band at $q = 0$ while Bragg-diffraction (blue double-headed arrow) excites particles from the ground band to the 1st excited band at $q = k_L$. For sufficiently deep lattice potentials, the local potentials become harmonic and the bands converge to the harmonic-oscillator eigenenergies.

2.3.4 Determination of molecular dynamical polarizability

Molecular dynamical polarizability can be determined from molecular response to the optical lattice potential. We measure the atomic and molecular Rabi oscillation frequencies at various lattice beam intensities using both Kapitza-Dirac and Bragg diffraction, see Fig. 2.7. These frequencies provide precise information on the energy dispersion, from which we extract the light shifts induced by the lattice potential. The lattice potential depth is proportional to the lattice intensity, $V_0 = \alpha_a I$, where $\alpha_a = \frac{\alpha}{2c\epsilon_0}$ is the dynamical polarizability of the atoms in a dipole trap and I is the lattice intensity. Since the lattice potential depths for atoms and molecules are different despite the lattice intensity being constant, this indicates that the atomic and molecular polarizabilities are not the same.

We first determine the atomic dynamical polarizability. The light shift on the cesium atoms in the ground state for far-detuned light U_{dip} can be expressed as the weighted sum of the contributions from the D_1 and D_2 lines [32], which gives

$$U_{\text{dip}} = - \left(f_1 \frac{3\pi c^2}{\omega_1^2} \frac{\Gamma_1}{\omega_1^2 - \omega_0^2} + f_2 \frac{3\pi c^2}{\omega_2^2} \frac{\Gamma_2}{\omega_2^2 - \omega_0^2} \right) I, \quad (2.25)$$

where $f_1 = 1/2.98$ and $f_2 = 1.98/2.98$ are the line strengths [33], $\omega_1 = 2\pi \times 335.116$ THz and $\omega_2 = 2\pi \times 351.726$ THz are the resonant frequencies, $\Gamma_1 = 2\pi \times 4.56$ MHz and $\Gamma_2 = 2\pi \times 5.22$ MHz are the natural line widths of the D_1 and D_2 lines, respectively. In addition, c is the speed of light. Contributions from other higher excited states are negligible.

For lattice beams with wavelength $\lambda = 1064$ nm, the optical frequency is $\omega_0 = 2\pi \times 281.760$ THz, and thus we obtain the atomic polarizability $\alpha_a = \frac{1.897 \times 10^{-38} (\text{C}\cdot\text{s})^2/\text{kg}}{2c\epsilon_0} = k_B \times 2.59 \text{ nK} \cdot \text{cm}^2/\text{W}$ from equating Eqs. (2.10) and (2.25), where the intensity is equivalent to $I = \left[(\sqrt{I_1} + \sqrt{I_2})^2 - 4\sqrt{I_2 I_2} \sin^2 \left(kz - \frac{\delta\omega t}{2} \right) \right]$. Since $V_0 = \alpha_a I$, the value of α_a allows us to evaluate the intensity of the optical lattice superimposed on the atoms directly from the measured lattice potential depth. We use these calibrated lattice intensities as a benchmark

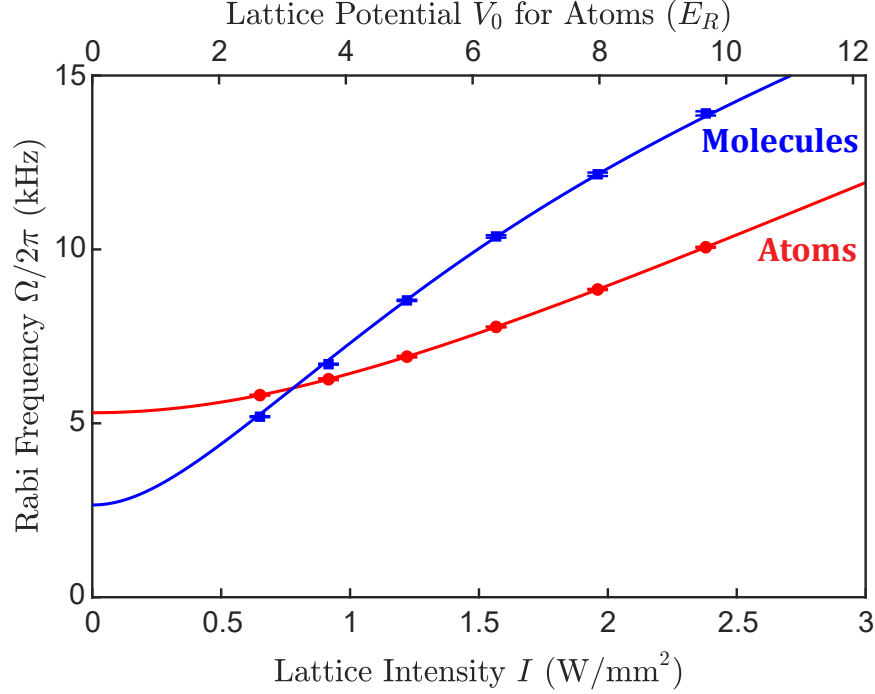


Figure 2.10: **Comparison of atomic and molecular polarizabilities.** From the Kapitza-Dirac diffraction measurements, we plot the atomic and molecular Rabi frequencies at various lattice intensities and their corresponding potential depths for atoms (in units of atomic recoil energy E_R). The lattice depth is extracted from the Rabi oscillations in which the Rabi frequency corresponds to the energy difference between the ground and 2nd excited band. The red solid line is an exact solution to the Mathieu equation for atoms while the blue solid line is a fit based on the solution to the Mathieu equation for molecules with an additional horizontal scaling factor. From fitting the data, we determine the molecular polarizability to be $\alpha_m = 1.95(2)\alpha_a = k_B \times 5.05(5) \text{ nK} \cdot \text{cm}^2/\text{W}$, where the atomic polarizability is $\alpha_a = k_B \times 2.59 \text{ nK} \cdot \text{cm}^2/\text{W}$.

to determine the molecular polarizability, since the lattice intensity is fixed for measurements on both atoms and molecules.

We compare the extracted lattice potential depths and their corresponding intensities for both atoms and molecules, see Table 2.3. From the calibrated lattice intensities and their induced light shifts on the molecules, we determine the molecular polarizability as $\alpha_m = k_B \times 5.05(5) \text{ nK} \cdot \text{cm}^2/\text{W}$ at $\lambda = 1064 \text{ nm}$. This is 1.95(2) times greater than the atomic polarizability α_a . We attribute the slight deviation from the expected ratio of $\alpha_m/\alpha_a \approx 2$ to the presence of additional molecular states accessible to Cs_2 molecules.

Table 2.3: **Comparison of atomic and molecular Rabi frequencies and their corresponding lattice potential depths** (in units of atomic recoil energy E_R) at different lattice intensities shown in Fig. 2.10.

Atoms			Molecules	
Lattice intensity	Frequency	Lattice depth	Frequency	Lattice depth
(W/mm ²)	$\Omega/2\pi$ (kHz)	V_0 (E_R)	$\Omega/2\pi$ (kHz)	V_0 (E_R)
0.65(1)	5.81(1)	2.65(4)	5.19(2)	5.06(2)
0.92(2)	6.27(3)	3.73(6)	6.70(1)	7.09(2)
1.22(1)	6.92(2)	4.96(4)	8.53(2)	9.64(3)
1.57(1)	7.77(1)	6.37(2)	10.37(4)	12.43(6)
1.96(1)	8.85(2)	7.98(3)	12.16(5)	15.53(9)
2.38(1)	10.06(1)	9.68(2)	13.91(6)	19.03(13)

Thus, our molecules experience a lattice potential twice as deep as that of atoms because their polarizabilities are nearly doubled, as confirmed by the Kapitza–Dirac diffraction measurements.

To summarize, we first load the atomic BEC into a 2D flat-bottomed optical trap, using microwave spectroscopy to confirm single-site loading. After loading, the magnetic field is ramped across the Feshbach resonance to initiate atom-molecule coupling. We probe the spatial coherence of atomic and molecular BECs by performing Kapitza–Dirac and Bragg diffraction using a 1D optical lattice. Both methods diffract particles into higher momentum modes, and the corresponding oscillation frequencies are used to calibrate the lattice potential depth. Molecules exhibit faster oscillations because of their larger dynamical polarizabilities.

CHAPTER 3

PHASE DOUBLING

In Chapter 1, we introduced the framework that characterizes reactions between coherent matter-wave fields as a nonlinear wave mixing process. In the following section, we examine how the phase evolves during this conversion process within the broader context of nonlinear optics.

3.1 Phase matching in second harmonic generation

Sufficiently intense laser light can be used to modify the optical properties of a material. The first example of this phenomenon was the discovery of second harmonic generation (SHG). In SHG, the response of the material scales quadratically with respect to the incident field. The incident field induces an array of oscillating dipole moments in the medium, collectively described by the polarization $\tilde{P}(t)$. The electric displacement field $\tilde{D}(t)$ inside the medium is given by

$$\tilde{D}(t) = \epsilon_0 \tilde{E}(t) + \tilde{P}(t), \quad (3.1)$$

where $\tilde{E}(t)$ is the incident electric field. Expanding $\tilde{P}(t)$ to higher orders gives us

$$\tilde{P}(t) = \epsilon_0 \left[\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \dots \right] \equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \dots, \quad (3.2)$$

where $\chi^{(1)}$ is the linear optical susceptibility and $\chi^{(2)}$ is the second order nonlinear optical susceptibility. When the electric field is set to $\tilde{E}(t) = E_0 e^{-i\omega_1 t} + E_0 e^{i\omega_1 t}$, the second order nonlinear polarization $\tilde{P}^{(2)}(t)$ becomes

$$\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t) = 2\epsilon_0 \chi^{(2)} E_0^2 (1 + \cos 2\omega_1 t). \quad (3.3)$$

Here, E_0 denotes the field amplitude and ω_1 is the optical frequency. The second term oscillating at $2\omega_1$ generates radiation at the second-harmonic frequency. Under the right conditions, SHG can transfer the power of the incident field at frequency ω_1 to radiation at the second-harmonic frequency $2\omega_1$ with minimal loss.

To understand this phenomenon, we solve the nonlinear wave equation

$$\nabla^2 \tilde{E} - \frac{\epsilon^{(1)}}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{1}{\epsilon c^2} \frac{\partial^2 \tilde{P}^{NL}}{\partial t^2}, \quad (3.4)$$

where $e^{(1)}(\omega) = 1 + \chi^{(1)}(\omega)$ and $\tilde{P}^{NL}$ is the nonlinear polarization [34]. We express the electric field as $\tilde{E}(z, t) = E_1 e^{i(k_1 z - \omega_1 t)} + E_2 e^{i(k_2 z - 2\omega_1 t)} + \text{c.c.}$ where E_1 and E_2 are redefined as the amplitudes of the incident and generated fields, and k_1 and k_2 are their corresponding wavevectors, respectively. Here, z denotes the position along the medium in the direction of beam propagation. Therefore, the second order nonlinear polarization term becomes

$$\tilde{P}^{NL} = \epsilon_0 \chi^{(2)} \tilde{E}^2 = \epsilon_0 \chi^{(2)} \left[E_1^2 e^{i(2k_1 z - 2\omega_1 t)} + 2E_1 E_2 e^{i(k_2 - k_1)z - \omega_1 t} + \text{c.c.} \right], \quad (3.5)$$

where terms oscillating at frequencies $3\omega_1$ and $4\omega_1$ have been omitted from $\tilde{E}^2$, since third and higher order nonlinear susceptibilities are not included in second order nonlinear polarization. Likewise, zero frequency static terms have also been omitted from $\tilde{E}^2$. Substituting $\tilde{E}$ and $\tilde{P}^{NL}$ into Eq. (3.4), we obtain

$$\begin{aligned} & \left(\frac{\partial^2 E_1}{\partial z^2} + 2ik_1 \frac{\partial E_1}{\partial z} - k_1^2 E_1 + \frac{\epsilon^{(1)}(\omega_1) \omega_1^2}{c^2} E_1 \right) e^{i(k_1 z - \omega_1 t)} \\ & + \left(\frac{\partial^2 E_2}{\partial z^2} + 2ik_2 \frac{\partial E_2}{\partial z} - k_2^2 E_2 + \frac{4\epsilon^{(1)}(2\omega_1) \omega_1^2}{c^2} E_2 \right) e^{i(k_2 z - 2\omega_1 t)} \\ & = - \frac{\chi^{(2)} \omega_1^2}{c^2} \left(4E_1^2 e^{i(2k_1 z - 2\omega_1 t)} + 2E_1 E_2 e^{i((k_2 - k_1)z - \omega_1 t)} \right). \end{aligned} \quad (3.6)$$

Since the dispersion relation of a monochromatic plane wave with wavevector k and frequency

ω in a medium is given by $k = \frac{n\omega}{c}$ where n is the linear refractive index, we can express k_1 and k_2 as $k_1 = \frac{n_1\omega_1}{c}$ and $k_2 = \frac{n_2 2\omega_1}{c}$ where $n_1^2 = \epsilon^{(1)}(\omega_1)$ and $n_2^2 = \epsilon^{(1)}(2\omega_1)$. Substituting these new definitions of $k_1^2 = \frac{\epsilon^{(1)}(\omega_1)\omega_1^2}{c^2}$ and $k_2^2 = \frac{4\epsilon^{(1)}(2\omega_1)\omega_1^2}{c^2}$ into Eq. (3.7), we obtain

$$\begin{aligned} & \left(\frac{\partial^2 E_1}{\partial z^2} + 2ik_1 \frac{\partial E_1}{\partial z} \right) e^{i(k_1 z - \omega_1 t)} + \left(\frac{\partial^2 E_2}{\partial z^2} + 2ik_2 \frac{\partial E_2}{\partial z} \right) e^{i(k_2 z - 2\omega_1 t)} \\ &= -\frac{\chi^{(2)}\omega_1^2}{c^2} \left(4E_1^2 e^{i(2k_1 z - 2\omega_1 t)} + 2E_1 E_2 e^{i((k_2 - k_1)z - \omega_1 t)} \right). \end{aligned} \quad (3.7)$$

Here, we can apply the slowly varying envelope approximation under the assumption that $\frac{\partial^2 E_1}{\partial z^2} \ll k_1 \frac{\partial E_1}{\partial z}$ and $\frac{\partial^2 E_2}{\partial z^2} \ll k_2 \frac{\partial E_2}{\partial z}$. Therefore, Eq. (3.7) simplifies to

$$\begin{aligned} & 2ik_1 \frac{\partial E_1}{\partial z} e^{ik_1 z} e^{-i\omega_1 t} + 2ik_2 \frac{\partial E_2}{\partial z} e^{ik_2 z} e^{-i2\omega_1 t} \\ &= -\frac{2\chi^{(2)}\omega_1^2}{c^2} E_1 E_2 e^{i(k_2 - k_1)z} e^{-i\omega_1 t} - \frac{4\chi^{(2)}\omega_1^2}{c^2} E_1^2 e^{i2k_1 z} e^{-i2\omega_1 t}. \end{aligned} \quad (3.8)$$

We can split Eq. (3.8) into separate equations for $e^{-i\omega_1 t}$ and $e^{-i2\omega_1 t}$

$$2ik_1 \frac{\partial E_1}{\partial z} e^{ik_1 z} = -\frac{2\chi^{(2)}\omega_1^2}{c^2} E_1 E_2 e^{i(k_2 - k_1)z} \quad (3.9)$$

$$2ik_2 \frac{\partial E_2}{\partial z} e^{ik_2 z} = -\frac{4\chi^{(2)}\omega_1^2}{c^2} E_1^2 e^{i2k_1 z}. \quad (3.10)$$

Reorganizing these equations, we arrive at

$$\begin{aligned} \frac{dE_1}{dz} &= \frac{i\omega_1 \chi^{(2)}}{n_1 c} E_1 E_2 e^{i\Delta k z} \\ \frac{dE_2}{dz} &= \frac{i\omega_1 \chi^{(2)}}{n_2 c} E_1^2 e^{-i\Delta k z}, \end{aligned} \quad (3.11)$$

where we have used $\Delta k = k_2 - 2k_1$, $k_1 = \frac{n_1\omega_1}{c}$ and $k_2 = \frac{2n_2\omega_1}{c}$. Setting E_1 as a constant

and integrating $\frac{dE_2}{dz}$ from $z = 0$ to L yields

$$E_2(L) = \frac{i\omega_1\chi^{(2)}}{n_2c}E_1^2 \int_0^L e^{-i\Delta kz} dz = \frac{i\omega_1\chi^{(2)}E_1^2}{n_2c} \frac{1 - e^{-i\Delta kL}}{i\Delta k}. \quad (3.12)$$

Substituting $I_i = \frac{1}{2}n_i\epsilon_0c|E_i|^2$ for $i = 1, 2$, we obtain

$$\begin{aligned} I_2 &= \frac{1}{2}n_2\epsilon_0c|E_2|^2 = \frac{2\epsilon_0\omega_1^2d_{eff}^2E_1^4}{n_2c}L^2\text{sinc}^2\left(\frac{\Delta kL}{2}\right) \\ I_1 &= \frac{1}{2}n_1\epsilon_0c|E_1|^2 = \frac{1}{2}n_1\epsilon_0cE_1^2, \end{aligned} \quad (3.13)$$

where we used $d_{eff} = \chi^{(2)}/2$. Therefore, the conversion efficiency I_2/I_1 is

$$\frac{I_2}{I_1} = \frac{4\omega_1^2d_{eff}^2E_0^2}{n_1n_2c^2}L^2\text{sinc}^2\left(\frac{\Delta kL}{2}\right). \quad (3.14)$$

When the phase mismatch between the incident and generated field vanishes ($\Delta k = 0$), the conversion efficiency approaches 100% and the generated power grows quadratically with the crystal length L – a condition referred to as *phase matching*. This follows from

$$L^2\text{sinc}^2\left(\frac{\Delta kL}{2}\right) = \frac{4}{\Delta k^2}\sin^2\left(\frac{\Delta kL}{2}\right) \approx \frac{4}{\Delta k^2}\left(\frac{\Delta kL}{2}\right)^2 = L^2, \quad (3.15)$$

for sufficiently small Δk . However, as the phase mismatch Δk increases, the sinc function suppresses the buildup of the generated field, leading to a reduction of conversion efficiency. To summarize, phase matching allows the generated field to build up constructively along the crystal, whereas phase mismatch causes these contributions to interfere destructively, reducing the overall conversion efficiency. When the incident fields propagate with the same wavevector, phase matching gives rise to *phase doubling* since $k_2 = 2k_1$. In the matter-wave picture, phase doubling is expected to occur when atoms are paired into molecules, since atoms occupying the same state share a common phase.

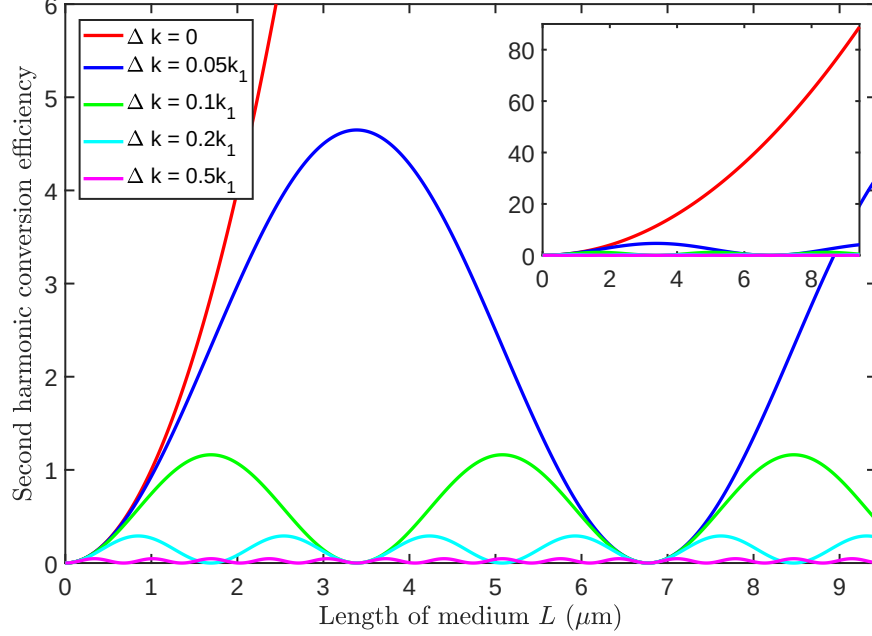


Figure 3.1: **Phase matching in second harmonic generation.** Perfect phase matching $\Delta k = 0$ yields maximum conversion efficiency and quadratic growth of the generated field with crystal length L . Increasing phase mismatch leads to suppression of the conversion process due to destructive interference and causes the generated power to oscillate with crystal length instead of increasing monotonically. Inset shows the monotonic increase of the generated power with crystal length when $\Delta k = 0$.

3.2 Spin model description of atom-molecule pairing

To show phase doubling, we imprint an arbitrary phase onto the atomic BEC using an optical lattice and monitor how this phase evolves when atoms are paired into molecules. The lattice resonantly couples the momentum states $|p = 0\rangle$ and $|2k_L\rangle$ where k_L is the lattice wavevector. Therefore, the system can be effectively described as a spin-1/2 system, with the two momentum states serving as the basis. In this section, we examine how this system evolves when atoms are paired into molecules, using the spin picture as our framework.

For a spin-1/2 system, the angular momentum operators are $S_i = \frac{\hbar}{2}\sigma_i$ where σ_i are the Pauli matrices for $i = x, y, z$. The rotation operator can be expressed as $\exp\left(-\frac{i}{\hbar}\mathbf{S} \cdot \hat{\mathbf{n}}\theta\right) = \exp\left(-\frac{i}{2}\boldsymbol{\sigma} \cdot \hat{\mathbf{n}}\theta\right)$ where $\hat{\mathbf{n}}$ is the unit vector and θ is the rotation angle. In 2×2 matrix form,

this becomes

$$\exp\left(-\frac{i}{2}\boldsymbol{\sigma} \cdot \hat{\mathbf{n}}\theta\right) = \begin{pmatrix} \cos\left(\frac{\theta}{2}\right) - in_z \sin\left(\frac{\theta}{2}\right) & (-in_x - n_y) \sin\left(\frac{\theta}{2}\right) \\ (-in_x + n_y) \sin\left(\frac{\theta}{2}\right) & \cos\left(\frac{\theta}{2}\right) + in_z \sin\left(\frac{\theta}{2}\right) \end{pmatrix} \quad (3.16)$$

The rotation operators rotate the Bloch vector on the Bloch sphere. Here, we define the pseudo-spin basis states as $|\uparrow\rangle = |p=0\rangle$ and $|\downarrow\rangle = |2k_L\rangle$. Starting from $|0\rangle$, rotating the Bloch vector around the x -axis gives us

$$\exp\left(-\frac{i}{2}\sigma_x\theta\right)|0\rangle = \begin{pmatrix} \cos\left(\frac{\theta}{2}\right) \\ -i \sin\left(\frac{\theta}{2}\right) \end{pmatrix} = \cos\left(\frac{\theta}{2}\right)|0\rangle - i \sin\left(\frac{\theta}{2}\right)|2k_L\rangle, \quad (3.17)$$

where $|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $|2k_L\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, and θ is the polar angle.

We can apply a similar treatment to spin-1 particles. The angular momentum matrices for spin-1 matrices are

$$J_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad J_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad J_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (3.18)$$

We use the following properties of these angular momentum operators to compute the rotations operators.

$$\left(\frac{J_x}{\hbar}\right)^n = \begin{cases} \frac{1}{2} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 1 \end{pmatrix} & n \in \{2m \mid m \in \mathbb{W}\}, \\ \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} & n \in \{2m+1 \mid m \in \mathbb{W}\}, \end{cases} \quad (3.19)$$

$$\left(\frac{J_y}{\hbar}\right)^n = \begin{cases} \frac{1}{2} \begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix} & n \in \{2m \mid m \in \mathbb{W}\}, \\ \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} & n \in \{2m+1 \mid m \in \mathbb{W}\}, \end{cases} \quad (3.20)$$

$$\left(\frac{J_z}{\hbar}\right)^n = \begin{cases} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & n \in \{2m \mid m \in \mathbb{W}\}, \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} & n \in \{2m+1 \mid m \in \mathbb{W}\}, \end{cases} \quad (3.21)$$

Therefore, the rotation operators can be evaluated as

$$\begin{aligned}
\exp\left(-\frac{iJ_x\theta}{\hbar}\right) &= 1 + \left(-\frac{iJ_x\theta}{\hbar}\right) + \frac{1}{2!}\left(-\frac{iJ_x\theta}{\hbar}\right)^2 + \frac{1}{3!}\left(-\frac{iJ_x\theta}{\hbar}\right)^3 + \frac{1}{4!}\left(-\frac{iJ_x\theta}{\hbar}\right)^4 + \frac{1}{5!}\left(-\frac{iJ_x\theta}{\hbar}\right)^5 + \dots \\
&= \left(1 - \frac{1}{2!}\left(\frac{J_x}{\hbar}\theta\right)^2 + \frac{1}{4!}\left(\frac{J_x}{\hbar}\theta\right)^4 - \dots\right) - i\left(\left(\frac{J_x}{\hbar}\theta\right) - \frac{1}{3!}\left(\frac{J_x}{\hbar}\theta\right)^3 + \frac{1}{5!}\left(\frac{J_x}{\hbar}\theta\right)^5 - \dots\right) \\
&= M_1 + \left(\frac{J_x}{\hbar}\right)^2 \left(1 - \frac{1}{2!}\theta^2 + \frac{1}{4!}\theta^4 - \dots\right) - i\left(\frac{J_x}{\hbar}\right) \left(\theta - \frac{1}{3!}\theta^3 + \frac{1}{5!}\theta^5 - \dots\right) \\
&= M_1 + \left(\frac{J_x}{\hbar}\right)^2 \cos\theta - i\left(\frac{J_x}{\hbar}\right) \sin\theta \\
&= \frac{1}{2} \begin{pmatrix} 1 + \cos\theta & -\sqrt{2}i \sin\theta & -1 + \cos\theta \\ -\sqrt{2}i \sin\theta & 2 \cos\theta & -\sqrt{2}i \sin\theta \\ -1 + \cos\theta & -\sqrt{2}i \sin\theta & 1 + \cos\theta \end{pmatrix}
\end{aligned} \tag{3.22}$$

$$\exp\left(-\frac{iJ_y\theta}{\hbar}\right) = M_2 + \left(\frac{J_y}{\hbar}\right)^2 \cos\theta - i\left(\frac{J_y}{\hbar}\right) \sin\theta = \frac{1}{2} \begin{pmatrix} 1 + \cos\theta & -\sqrt{2} \sin\theta & 1 - \cos\theta \\ \sqrt{2} \sin\theta & 2 \cos\theta & -\sqrt{2} \sin\theta \\ 1 - \cos\theta & \sqrt{2} \sin\theta & 1 + \cos\theta \end{pmatrix} \tag{3.23}$$

$$\exp\left(-\frac{iJ_z\theta}{\hbar}\right) = M_3 + \left(\frac{J_z}{\hbar}\right)^2 \cos\theta - i\left(\frac{J_z}{\hbar}\right) \sin\theta = \begin{pmatrix} e^{-i\theta} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{i\theta} \end{pmatrix}, \tag{3.24}$$

where we have used

$$M_1 = \frac{1}{2} \begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix}, \quad M_2 = \frac{1}{2} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix}, \quad M_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3.25}$$

Starting from $|0\rangle$, applying the $\exp\left(-\frac{iJ_x\theta}{\hbar}\right)$ rotation operator gives us

$$\begin{aligned}
\exp\left(-\frac{iJ_x\theta}{\hbar}\right)|0\rangle_s &= \frac{1}{2} \begin{pmatrix} 1 + \cos\theta & -\sqrt{2}i \sin\theta & -1 + \cos\theta \\ -\sqrt{2}i \sin\theta & 2 \cos\theta & -\sqrt{2}i \sin\theta \\ -1 + \cos\theta & -\sqrt{2}i \sin\theta & 1 + \cos\theta \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 + \cos\theta \\ -\sqrt{2}i \sin\theta \\ -1 + \cos\theta \end{pmatrix} \\
&= \frac{1}{2}(1 + \cos\theta)|0\rangle_s - \frac{i}{\sqrt{2}}\sin\theta|2k_L\rangle_s - \frac{1}{2}(1 - \cos\theta)|4k_L\rangle_s \\
&= \cos^2\left(\frac{\theta}{2}\right)|0\rangle_s - \frac{i}{\sqrt{2}}\sin\theta|2k_L\rangle_s - \sin^2\left(\frac{\theta}{2}\right)|4k_L\rangle_s,
\end{aligned} \tag{3.26}$$

where we have used $|0\rangle_s = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$, $|2k_L\rangle_s = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$, and $|4k_L\rangle_s = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$.

We can now extend this framework to describe atom-molecule pairing. We define the molecular wavefunction ψ_m as the product of two atomic wavefunctions ψ_a . By defining the atomic wavefunction as $\psi_a = \cos\frac{\theta}{2}|0\rangle - i\sin\frac{\theta}{2}|2k_L\rangle$, the molecular wavefunction becomes

$$\begin{aligned}
\psi_m = \psi_a^2 &= \cos^2\left(\frac{\theta}{2}\right)|0\rangle|0\rangle - i\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)|0\rangle|2k_L\rangle \\
&\quad - i\sin\left(\frac{\theta}{2}\right)\cos\left(\frac{\theta}{2}\right)|2k_L\rangle|0\rangle - \sin^2\left(\frac{\theta}{2}\right)|2k_L\rangle|2k_L\rangle.
\end{aligned} \tag{3.27}$$

Since the pairs $|0\rangle_s$ and $|0\rangle|0\rangle$, $|2k_L\rangle_s$ and $|0\rangle|2k_L\rangle$ (or $|2k_L\rangle|0\rangle$), and $|4k_L\rangle_s$ and $|2k_L\rangle|2k_L\rangle$ represent the same momentum modes, but reside in Hilbert spaces of different dimensionality, we apply a transformation operator $\hat{U}_1$ that projects the two-qubit Hilbert space onto the spin-1 manifold. This transformation operator is expressed as

$$\hat{U}_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{3.28}$$

Here, the factor of $\frac{1}{\sqrt{2}}$ comes from bosonic symmetrization $\frac{1}{\sqrt{2}}(|0\rangle|2k_L\rangle + |2k_L\rangle|0\rangle)$. By applying $\hat{U}_1$ to ψ_m , we obtain

$$\begin{aligned}\hat{U}_1\psi_m &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos^2 \frac{\theta}{2} \\ -i \sin \frac{\theta}{2} \cos \frac{\theta}{2} \\ -i \sin \frac{\theta}{2} \cos \frac{\theta}{2} \\ -\sin^2 \frac{\theta}{2} \end{pmatrix} = \begin{pmatrix} \cos^2 \frac{\theta}{2} \\ -\frac{i}{\sqrt{2}} \sin \theta \\ -\sin^2 \frac{\theta}{2} \end{pmatrix} \\ &= \cos^2 \left(\frac{\theta}{2} \right) |0\rangle_s - \frac{i}{\sqrt{2}} \sin \theta |2k_L\rangle_s - \sin^2 \left(\frac{\theta}{2} \right) |4k_L\rangle_s,\end{aligned}\tag{3.29}$$

which is consistent with the molecular wavefunction in Eq. (3.26). Thus, the process of atom-molecule pairing reflects the transition from a spin-1/2 to a spin-1 system. The atomic population fractions n_0 and n_2 corresponding to momentum $p = 0$ and $2k_L$, respectively, are given by

$$n_0 = |\langle 0|\psi_a\rangle|^2 = \cos^2 \frac{\theta}{2}\tag{3.30}$$

$$n_2 = |\langle 2k_L|\psi_a\rangle|^2 = \sin^2 \frac{\theta}{2},\tag{3.31}$$

while the molecular population fractions m_0 , m_2 and m_4 corresponding to momentum $p = 0$, $2k_L$ and $4k_L$, respectively, are given by

$$m_0 = |_s\langle 0|\psi_m\rangle|^2 = \cos^4 \frac{\theta}{2} = n_0^2\tag{3.32}$$

$$m_2 = |_s\langle 2k_L|\psi_m\rangle|^2 = \frac{1}{2} \sin^2 \theta = 2n_0 n_2\tag{3.33}$$

$$m_4 = |_s\langle 4k_L|\psi_m\rangle|^2 = \sin^4 \frac{\theta}{2} = n_2^2.\tag{3.34}$$

3.3 Atom-molecule many-body Hamiltonian with Bragg coupling

We can model the full atom-molecule pairing process using the many-body Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_I$ where

$$\hat{H}_0 = \epsilon_0 \hat{a}_0^\dagger \hat{a}_0 + \epsilon_2 \hat{a}_2^\dagger \hat{a}_2 + \left(\nu + \frac{\epsilon_0}{2}\right) \hat{m}_0^\dagger \hat{m}_0 + \left(\nu + \frac{\epsilon_2}{2}\right) \hat{m}_2^\dagger \hat{m}_2 + \left(\nu + \frac{\epsilon_4}{2}\right) \hat{m}_4^\dagger \hat{m}_4 \quad (3.35)$$

$$\begin{aligned} \hat{H}_I &= \frac{\hbar\Omega_a}{2} (\hat{a}_2^\dagger \hat{a}_0 + \hat{a}_0^\dagger \hat{a}_2) + \hbar\gamma (\hat{m}_0^\dagger \hat{a}_0^2 + \hat{a}_0^{\dagger 2} \hat{m}_0 + \hat{m}_4^\dagger \hat{a}_2^2 + \hat{a}_2^{\dagger 2} \hat{m}_4) \\ &\quad + \hbar\gamma_2 (\hat{m}_2^\dagger \hat{a}_0 \hat{a}_2 + \hat{m}_2^\dagger \hat{a}_2 \hat{a}_0 + \hat{a}_0^\dagger \hat{a}_2^\dagger \hat{m}_2 + \hat{a}_2^\dagger \hat{a}_0^\dagger \hat{m}_2) \\ &= \frac{\hbar\Omega_a}{2} (\hat{a}_2^\dagger \hat{a}_0 + \hat{a}_0^\dagger \hat{a}_2) + \hbar\gamma (\hat{m}_0^\dagger \hat{a}_0^2 + \hat{a}_0^{\dagger 2} \hat{m}_0 + \hat{m}_4^\dagger \hat{a}_2^2 + \hat{a}_2^{\dagger 2} \hat{m}_4) + 2\hbar\gamma_2 (\hat{m}_2^\dagger \hat{a}_0 \hat{a}_2 + \hat{a}_0^\dagger \hat{a}_2^\dagger \hat{m}_2) \end{aligned} \quad (3.36)$$

where the kinetic energies are given by $\epsilon_0 = 0$, $\epsilon_2 = 4E_R$ and $\epsilon_4 = 16E_R$, with E_R as the lattice recoil energy. Here, we replaced the atomic field operators with $\hat{a}_\kappa^\dagger$ and $\hat{a}_\kappa$ instead of $\hat{\psi}_a^\dagger$ and $\hat{\psi}_a$, and molecular field operators with $\hat{m}_\kappa^\dagger$ and $\hat{m}_\kappa$ instead of $\hat{\psi}_m^\dagger$ and $\hat{\psi}_m$, where κ are the dimensionless momenta in units of k_L . In addition, ν is the detuning between the closed channel molecular state and open channel atomic threshold, Ω_a is the atomic Rabi frequency induced by Bragg coupling and γ_2 is the atom-molecule coupling strength between $p = 0$ and $2k_L$. Since $\epsilon_0 = 0$, $\hat{H}_0$ reduces to

$$\hat{H}_0 = \epsilon_2 \hat{a}_2^\dagger \hat{a}_2 + \nu \hat{m}_0^\dagger \hat{m}_0 + \left(\nu + \frac{\epsilon_2}{2}\right) \hat{m}_2^\dagger \hat{m}_2 + \left(\nu + \frac{\epsilon_4}{2}\right) \hat{m}_4^\dagger \hat{m}_4. \quad (3.37)$$

In the interaction picture, the Hamiltonian becomes $\hat{H}_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{H}_I e^{-i\hat{H}_0 t/\hbar}$. To evaluate this expression, we consider a few illustrative examples. When we evaluate $e^{i\hat{H}_0 t/\hbar} \hat{a}_2^\dagger \hat{a}_0 e^{-i\hat{H}_0 t/\hbar}$, this expression separates into

$$e^{i\hat{H}_0 t/\hbar} \hat{a}_2^\dagger \hat{a}_0 e^{-i\hat{H}_0 t/\hbar} = \left(e^{i\hat{H}_0 t/\hbar} \hat{a}_2^\dagger e^{-i\hat{H}_0 t/\hbar}\right) \left(e^{i\hat{H}_0 t/\hbar} \hat{a}_0 e^{-i\hat{H}_0 t/\hbar}\right), \quad (3.38)$$

so we can treat each operator separately. We expand the first parenthesis as

$$e^{i\hat{H}_0 t/\hbar} \hat{a}_2^\dagger e^{-i\hat{H}_0 t/\hbar} = \hat{a}_2^\dagger + \frac{i\epsilon_2 t}{\hbar} [\hat{H}_0, \hat{a}_2^\dagger] + \frac{1}{2!} \left(\frac{i\epsilon_2 t}{\hbar} \right)^2 [\hat{H}_0, [\hat{H}_0, \hat{a}_2^\dagger]] + \dots, \quad (3.39)$$

using the Baker-Campbell-Hausdorff formula. Since $[\hat{a}_2^\dagger \hat{a}_2, \hat{a}_2^\dagger] = \hat{a}_2^\dagger$ and $[\hat{m}_0^\dagger \hat{m}_0, \hat{a}_2^\dagger] = [\hat{m}_2^\dagger \hat{m}_2, \hat{a}_2^\dagger] = [\hat{m}_4^\dagger \hat{m}_4, \hat{a}_2^\dagger] = 0$, Eq. (3.39) simplifies to

$$e^{i\hat{H}_0 t/\hbar} \hat{a}_2^\dagger e^{-i\hat{H}_0 t/\hbar} = \hat{a}_2^\dagger \left(1 + \frac{i\epsilon_2 t}{\hbar} + \frac{1}{2!} \left(\frac{i\epsilon_2 t}{\hbar} \right)^2 + \dots \right) = \hat{a}_2^\dagger e^{\frac{i\epsilon_2 t}{\hbar}}. \quad (3.40)$$

We obtain $e^{i\hat{H}_0 t/\hbar} \hat{a}_0 e^{-i\hat{H}_0 t/\hbar} = \hat{a}_0$ in a similar manner. Therefore, Eq. (3.38) becomes

$$e^{i\hat{H}_0 t/\hbar} \hat{a}_2^\dagger \hat{a}_0 e^{-i\hat{H}_0 t/\hbar} = \hat{a}_2^\dagger \hat{a}_0 e^{i\epsilon_2 t/\hbar}. \quad (3.41)$$

Repeating the calculations for the rest of the operators in H_I gives us

$$\begin{aligned} \hat{H}_I(t) &= \hat{H}_{I,\text{Bragg}} + \hat{H}_{I,\text{pair}} \\ &= \frac{\hbar\Omega_a}{2} \left(\hat{a}_2^\dagger \hat{a}_0 e^{i4E_R t/\hbar} + \hat{a}_0^\dagger \hat{a}_2 e^{-i4E_R t/\hbar} \right) \\ &\quad + \hbar\gamma \left(\hat{m}_0^\dagger \hat{a}_0^2 e^{i\nu t/\hbar} + \hat{a}_0^\dagger{}^2 \hat{m}_0 e^{-i\nu t/\hbar} + \hat{m}_4^\dagger \hat{a}_2^2 e^{i\nu t/\hbar} + \hat{a}_2^\dagger{}^2 \hat{m}_4 e^{-i\nu t/\hbar} \right) \\ &\quad + 2\hbar\gamma_2 \left(\hat{m}_2^\dagger \hat{a}_0 \hat{a}_2 e^{i(\nu-2E_R)t/\hbar} + \hat{a}_0^\dagger \hat{a}_2^\dagger \hat{m}_2 e^{-i(\nu-2E_R)t/\hbar} \right), \end{aligned} \quad (3.42)$$

where $\hat{H}_{I,\text{Bragg}}$ contains the term with the Rabi coupling strength $\frac{\hbar\Omega_a}{2}$ and $\hat{H}_{I,\text{pair}}$ contains the terms with coupling strengths $\hbar\gamma$ and $\hbar\gamma_2$. Using Eq. (3.42), we derive the equations of motion for $\hat{M}_0 = \hat{m}_0^\dagger \hat{m}_0$, $\hat{M}_2 = \hat{m}_2^\dagger \hat{m}_2$ and $\hat{M}_4 = \hat{m}_4^\dagger \hat{m}_4$. With the help of the following Leibniz rules for operators $\hat{A}$, $\hat{B}$, $\hat{C}$ and $\hat{D}$

$$[\hat{A}\hat{B}, \hat{C}\hat{D}] = \hat{A} [\hat{B}, \hat{C}] \hat{D} + \hat{A}\hat{C} [\hat{B}, \hat{D}] + [\hat{A}, \hat{C}] \hat{D}\hat{B} + \hat{C} [\hat{A}, \hat{D}] \hat{B} \quad (3.43)$$

$$\begin{aligned}
[\hat{A}\hat{B}\hat{C}, \hat{D}\hat{E}] = & \hat{A}\hat{B} [\hat{C}, \hat{D}] \hat{E} + \hat{A} [\hat{B}, \hat{D}] \hat{C}\hat{E} + [\hat{A}, \hat{D}] \hat{B}\hat{C}\hat{E} \\
& + \hat{D}\hat{A}\hat{B} [\hat{C}, \hat{E}] + \hat{D}\hat{A} [\hat{B}, \hat{E}] \hat{C} + \hat{D} [\hat{A}, \hat{E}] \hat{B}\hat{C},
\end{aligned} \tag{3.44}$$

the equations of motion for $\hat{M}_0$, $\hat{M}_2$ and $\hat{M}_4$ become

$$\partial_t \hat{M}_0 = \frac{i}{\hbar} [\hat{H}_{I,\text{pair}}, \hat{M}_0] = -i\gamma \left(\hat{m}_0^\dagger \hat{a}_0^2 e^{i\nu t/\hbar} - \hat{a}_0^{\dagger 2} \hat{m}_0 e^{-i\nu t/\hbar} \right), \tag{3.45}$$

$$\partial_t \hat{M}_2 = \frac{i}{\hbar} [\hat{H}_{I,\text{pair}}, \hat{M}_2] = -2i\gamma_2 \left(\hat{m}_2^\dagger \hat{a}_0 \hat{a}_2 e^{i(\nu-2E_R)t/\hbar} - \hat{a}_0^\dagger \hat{a}_2^\dagger \hat{m}_2 e^{-i(\nu-2E_R)t/\hbar} \right), \tag{3.46}$$

$$\partial_t \hat{M}_4 = \frac{i}{\hbar} [\hat{H}_{I,\text{pair}}, \hat{M}_4] = -i\gamma \left(\hat{m}_4^\dagger \hat{a}_2^2 e^{i\nu t/\hbar} - \hat{a}_2^{\dagger 2} \hat{m}_4 e^{-i\nu t/\hbar} \right). \tag{3.47}$$

Approximating the field operators with complex amplitudes, $\hat{a}_0 \rightarrow \sqrt{N_0} e^{i\varphi_{a0}}$ and $\hat{m}_0 \rightarrow \sqrt{M_0} e^{i\varphi_{m0}}$, $\hat{a}_2 \rightarrow \sqrt{N_2} e^{i\varphi_{a2}}$ and $\hat{m}_2 \rightarrow \sqrt{M_2} e^{i\varphi_{m2}}$, and $\hat{m}_4 \rightarrow \sqrt{M_4} e^{i\varphi_{m4}}$, we obtain

$$\partial_t M_0 = 2\gamma N_0 \sqrt{M_0} \sin \left(\frac{\nu t}{\hbar} + 2\varphi_{a0} - \varphi_{m0} \right), \tag{3.48}$$

$$\partial_t M_2 = 4\gamma_2 \sqrt{N_0 N_2} \sqrt{M_2} \sin \left(\frac{(\nu - 2E_R)t}{\hbar} + \varphi_{a0} + \varphi_{a2} - \varphi_{m2} \right), \tag{3.49}$$

$$\partial_t M_4 = 2\gamma N_2 \sqrt{M_4} \sin \left(\frac{\nu t}{\hbar} + 2\varphi_{a2} - \varphi_{m4} \right). \tag{3.50}$$

Assuming N_0 and N_2 are constant at small t , solving for M_0 , M_2 and M_4 under the initial conditions $M_0(0) = 0$, $M_2(0) = 0$ and $M_4(0) = 0$ gives us

$$M_0 = \left(\frac{\hbar\gamma N_0}{\nu} \right)^2 \left[\cos \varphi'_R - \cos \left(\frac{\nu t}{\hbar} + \varphi'_R \right) \right]^2, \tag{3.51}$$

$$M_2 = \left(\frac{2\hbar\gamma_2 \sqrt{N_0 N_2}}{\nu - 2E_R} \right)^2 \left[\cos \varphi''_R - \cos \left(\frac{(\nu - 2E_R)t}{\hbar} + \varphi''_R \right) \right]^2, \tag{3.52}$$

$$M_4 = \left(\frac{\hbar\gamma N_2}{\nu} \right)^2 \left[\cos \varphi'''_R - \cos \left(\frac{\nu t}{\hbar} + \varphi'''_R \right) \right]^2, \tag{3.53}$$

where $\varphi'_R = 2\varphi_{a_0} - \varphi_{m_0}$, $\varphi''_R = \varphi_{a_0} + \varphi_{a_2} - \varphi_{m_2}$ and $\varphi'''_R = 2\varphi_{a_2} - \varphi_{m_2}$. Assuming $\varphi'_R = \varphi''_R = \varphi'''_R = \varphi_R = \pi/2$, M_0 , M_2 and M_4 can be approximated at small t as

$$M_0(t) = \left(\frac{\hbar\gamma N_0}{\nu} \right)^2 \sin^2 \left(\frac{\nu t}{\hbar} \right) \approx \gamma^2 N_0^2 t^2 \quad (3.54)$$

$$M_2(t) = \left(\frac{2\hbar\gamma_2\sqrt{N_0 N_2}}{\nu - 2E_R} \right)^2 \sin^2 \left(\frac{(\nu - 2E_R)t}{\hbar} \right) \approx 4\gamma_2^2 N_0 N_2 t^2 \quad (3.55)$$

$$M_4(t) = \left(\frac{\hbar\gamma N_2}{\nu} \right)^2 \sin^2 \left(\frac{\nu t}{\hbar} \right) \approx \gamma^2 N_2^2 t^2. \quad (3.56)$$

These equations mirror Eqs. (3.32), (3.33) and (3.34) with the exception of the factor of four in Eq. (3.55). Eqs. (3.54)–(3.56) yield a population ratio of $M_0 : M_2 : M_4 = 1 : 4 : 1$ whereas Eqs. (3.32)–(3.34) yield $m_0 : m_2 : m_4 = 1 : 2 : 1$ for $N_0/N_2 = n_0/n_2 = 1$ and $\gamma_2 = \gamma$. We address this discrepancy in the following chapter. Furthermore, Eqs. (3.54)–(3.56) treat N_0 and N_2 as constants, whereas both parameters are dynamical variables in the actual system. A full treatment requires coupled equations for both atomic and molecular populations.

3.4 Experimental detection of matter-wave phases

We imprint a phase pattern onto the atomic BEC by pulsing on a moving optical lattice with intensity $I(x, t) = I_0 \sin^2 k_L(x - v_L t)$, where $v_L = \delta\omega/2k_L = \hbar k_L/m$ is the recoil velocity, m is the mass of the ^{133}Cs atom and $\delta\omega = 4E_R$. The lattice potential depth is set to $3.63(1) E_R$, just weak enough to only couple $|p=0\rangle$ and $|2k_L\rangle$. After the Bragg pulse, we shut off the optical lattice and immediately convert the atoms into molecules in 1.5 ms. Any remaining atoms are blown away with a resonant light pulse. When we blow away the atoms, we simultaneously shut off the DMD potential and let the molecules expand in free space for 16 ms. The dipole trap is left turned on in the z -direction so that the molecules only expand in the x and y directions. We dissociate the molecules into atoms at the end of this time-of-flight and image the atoms.

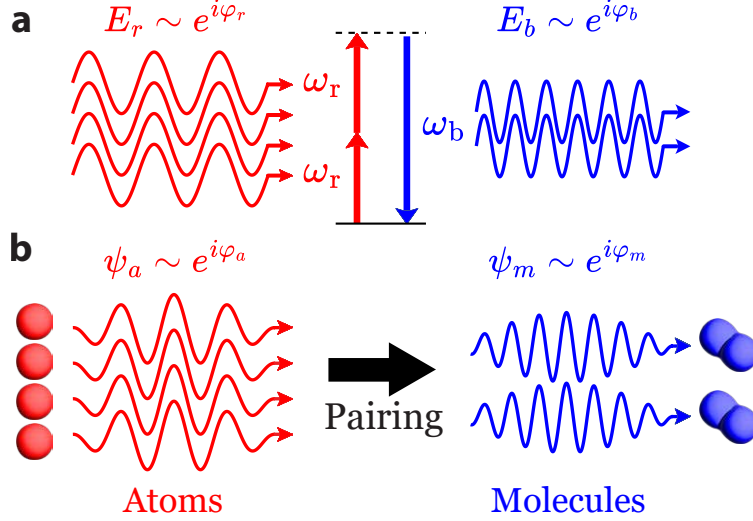


Figure 3.2: **Phase doubling in nonlinear optics and matter-wave reactions.** **a**, Phase doubling in a nonlinear crystal $\varphi_b = 2\varphi_r$. In the perfect phase matching scenario, pairs of red photons with momentum $k_r = \nabla\varphi_r$ and frequency $\omega_r = -\partial_t\varphi_r$ are converted into blue photons with twice the momentum $k_b = 2k_r$ and frequency $\omega_b = 2\omega_r$. **b**, In the matter-wave analogue, atoms (red spheres) with wave function ψ_a and phase φ_a are converted into diatomic molecules (blue spheres) with wave function ψ_m and phase φ_m . Phase doubling $\varphi_m = 2\varphi_a$ arises from phase matching, as the atomic phases add constructively through the nonlinear wave mixing process.

The Bragg pulse imprints phase pattern $\varphi_a(x)$ on the atomic wavefunction $\psi_a(x) = \sqrt{\rho_a(x)}e^{i\varphi_a(x)}$. Following the pulse, as atoms are paired into molecules, $\varphi_a(x)$ transforms into $\varphi_m(x)$ of the molecular wavefunction $\psi_m(x) = \sqrt{\rho_m(x)}e^{i\varphi_m(x)}$. Here ρ_a and ρ_m are the atomic and molecular densities. The scheme is illustrated in Fig. 3.3a.

For diffracted atoms, the single particle wavefunction $\psi_a(x) = \psi_{a0} + \psi_{a2}e^{2ik_Lx} = \cos(\Omega_a t/2) - i \sin(\Omega_a t/2)e^{2ik_Lx}$ can be modeled by a two-level system undergoing Rabi oscillations with frequency Ω_a . In the Bloch-sphere representation, the polar angle evolves as $\theta = \Omega_a t$. The pairing of atoms in two momentum states results in molecules occupying three momentum states which is described by the wavefunction $\psi_m(x) = \psi_{m0} + \psi_{m2}e^{2ik_Lx} + \psi_{m4}e^{4ik_Lx}$. Molecules with momentum $k = 0$ and $4k_L$ come from pairing atoms with the same momentum $k = 0$ or $2k_L$, the matter-wave analogue of second harmonic generation (SHG). The molecular populations scale as $m_0 \propto \gamma^2 n_0^2$ and $m_4 \propto \gamma^2 n_2^2$, where $n_0 = |\psi_{a0}|^2$ and

$n_2 = |\psi_{a_2}|^2$. Molecules with momentum $k = 2k_L$ come from pairing atoms with distinct momenta $k = 0$ and $2k_L$, the matter-wave analogue of sum frequency generation (SFG). The $k = 2k_L$ population scales as $m_2 \propto 4\gamma_2^2 n_0 n_2$. From these equations, we can reconstruct the molecular wavefunction as

$$\psi_m(x, t) = A_m \left(\gamma \cos^2 \frac{\Omega_a t}{2} - i\gamma_2 \sin \Omega_a t e^{2ik_L x} - \gamma \sin^2 \frac{\Omega_a t}{2} e^{4ik_L x} \right), \quad (3.57)$$

where $A_m = [\gamma^2 + (\gamma_2^2 - \gamma^2/2) \sin^2 \Omega_a t]^{-1/2}$ is the normalization constant. When $\gamma_2/\gamma = 1/\sqrt{2}$, we recover Eq. (3.26). Therefore, the normalized molecular population fractions are

$$m_0 = A_m^2 \gamma^2 \cos^4 \frac{\Omega_a t}{2} \quad (3.58)$$

$$m_2 = A_m^2 \gamma_2^2 \sin^2 \Omega_a t \quad (3.59)$$

$$m_4 = A_m^2 \gamma^2 \sin^4 \frac{\Omega_a t}{2}. \quad (3.60)$$

We measure the molecular populations after time-of-flight expansion. The populations m_0 and m_4 oscillate at the Rabi frequency Ω_a . They reach unity when atoms occupy a single momentum state after $0, \pi, 2\pi, \dots$ Bragg pulses. On the other hand, the population m_2 oscillates at twice the Rabi frequency $2\Omega_a$ and reaches the maximum $A_2 = 0.58(1)$ after $\pi/2, 3\pi/2, \dots$ Bragg pulses, see Figs. 3.3b and c. A decoherence rate η is added to describe the weak decay in the oscillation amplitudes. The results from the fitting are listed in Table 3.1.

Our model accurately describes the measurement results, yielding a coupling constant ratio of $\gamma_2/\gamma = 0.82(3)$. The detuning of sum-frequency generation $\delta E = -2E_R = -h \times 2.7$ kHz with respect to the molecular bound state is non-negligible compared to the resonance strength $\Gamma = \delta\mu\Delta B = h \times 6.3(5)$ kHz of the g -wave Feshbach resonance, calculated from the resonance width $\Delta B = 8.3(5)$ mG and relative magnetic moment $\delta\mu = h \times 0.76(3)$ MHz/G. We can estimate the reduced coupling strength from the Lorentzian lineshape, $(\gamma_2/\gamma)^2 = 1/(1 + (\delta E)^2/(\Gamma/2)^2) = 1/(1 + 4\delta E^2/\Gamma^2)$, which gives us $\gamma_2/\gamma \approx 0.77(3)$, consistent with our

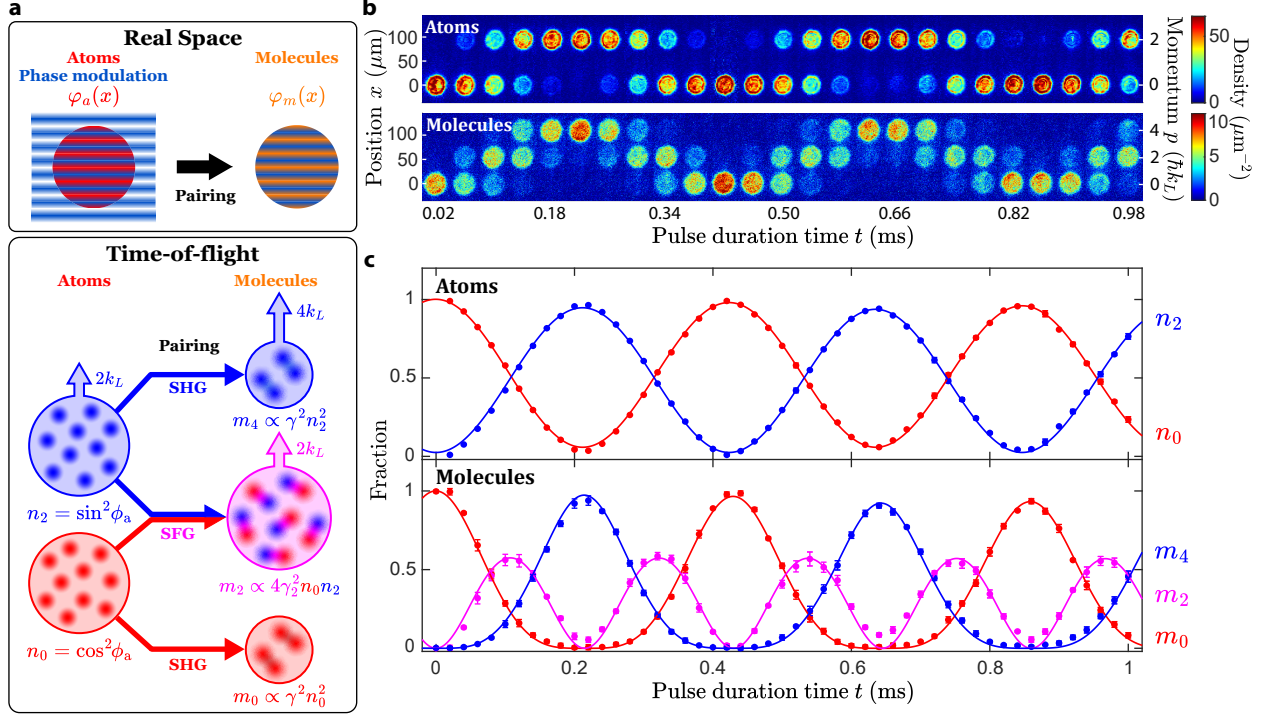


Figure 3.3: **Phase modulation on atomic and molecular BECs.** **a**, Experimental protocol. A Bragg diffraction pulse imprints a phase $\varphi_a(x)$ onto the atomic BEC. The atomic BEC is then converted into a molecular BEC with phase $\varphi_m(x)$. The imprinted phase is reflected in the populations of diffracted atoms, $n_0 = \cos^2 \phi_a$ and $n_2 = \sin^2 \phi_a$. After pairing, molecules occupy momenta $k = 0, 2k_L$ and $4k_L$ which are proportional to the products of atomic populations. The molecular fractions of m_0 and m_4 are generated by second harmonic generation (SHG) with coupling constant γ while m_2 is generated by sum frequency generation (SFG) with γ_2 . The factor of four in m_2 comes from bosonic exchange symmetry. **b**, Oscillations of momentum state populations as a result of phase modulation on the atomic and molecular BECs. Images are taken after 16 ms time-of-flight expansion. Images shown here are averaged over five independent measurements. We note that the diffracted molecules move at half the speed of the atoms since they are twice as massive. **c**, Population fractions of diffracted atoms and molecules. Atomic fractions of n_0 and n_2 oscillate at a Rabi frequency of $\Omega_a = 2\pi \times 2.36(1)$ kHz. Molecular fractions are fit using $m_0 = \cos^4 \Omega_0 t/2$, $m_2 = A_2 \sin^2 \Omega_2 t/2$ and $m_4 = \sin^4 \Omega_4 t/2$, which give $\Omega_0 = 2\pi \times 2.33(1)$, $\Omega_2 = 2\pi \times 4.66(1)$, and $\Omega_4 = 2\pi \times 2.33(1)$ kHz, respectively and $A_2 = 0.58(1)$. Error bars show 1- σ standard deviations of the means.

observed value $\gamma_2/\gamma = 0.82(3)$. Thus, the reduced sum-frequency coupling strength $\gamma_2 < \gamma$ is consistent with our expectation that the atom-molecule conversion is suppressed due to the energetic mismatch of δE between the atomic pair and the molecular bound state.

The phase information of the atomic and molecular matter waves can be readily extracted

Table 3.1: **Oscillation frequencies and decoherence rates of the atomic and molecular populations.** Obtained from the fits in Figs. 3.3c.

Atoms			Molecules		
Momentum	Frequency	Decay rate	Momentum	Frequency	Decay rate
k	$\Omega/2\pi$ (kHz)	η (ms ⁻¹)	k	$\Omega/2\pi$ (kHz)	η (ms ⁻¹)
0	2.36(1)	0.05(1)	0	2.33(1)	0.08(1)
$2k_L$	2.36(1)	0.03(1)	$2k_L$	4.66(1)	0.03(2)
			$4k_L$	2.33(1)	0.13(2)

from their diffraction patterns. To see this, we express the general wavefunction $\psi(x)$ as

$$\psi(x) = \sqrt{\rho(x)}e^{i\varphi(x)} = \sum_{j=0,\pm1,\pm2\dots} \psi_{s2j} e^{2ijk_L x}, \quad s \in \{a, m\} \quad (3.61)$$

where $\rho(x)$ is the particle density and ψ_{s2j} is the amplitude of the plane wave with momentum $2jk_L$, for $s \in \{a, m\}$. We evaluate the phase modulation amplitude ϕ_a at the antinodes of the lattice $\phi_a \equiv \varphi_a(x = \lambda/4)$. In the co-moving lattice frame, this phase evolves at a rate given by the Rabi frequency, $\dot{\phi}_a = \Omega_{at}/2$.

However, we need a general expression for extracting the molecular phase, since it's not guaranteed that $\phi_m = 2\phi_a$ once the lattice is turned off and atoms are paired into molecules, where ϕ_m is the phase modulation amplitude on the molecules. We can rewrite Eq. (3.61) for atoms as

$$\sqrt{\rho_a(x)}e^{i\phi_a} = \cos\left(\frac{\theta}{2}\right) - i \sin\left(\frac{\theta}{2}\right) e^{2ik_L x}. \quad (3.62)$$

We can expand Eq. (3.62) as

$$\sqrt{\rho_a(x)}(\cos \phi_a + i \sin \phi_a) = \cos\left(\frac{\theta}{2}\right) - i \sin\left(\frac{\theta}{2}\right) (\cos 2k_L x + i \sin 2k_L x). \quad (3.63)$$

Organizing Eq. (3.63) into real and imaginary parts, dividing $\cos \phi_a$ by $\sin \phi_a$ gives us

$$\cot \phi_a = \frac{\cos \phi_a}{\sin \phi_a} = \frac{\cos \frac{\theta}{2} + \sin \frac{\theta}{2} \sin 2k_L x}{-\sin \frac{\theta}{2} \cos 2k_L x}. \quad (3.64)$$

By substituting $x = \lambda/4$ into Eq. (3.64) and using $n_0 = \cos^2 \frac{\theta}{2}$ and $n_2 = \sin^2 \frac{\theta}{2}$, we can extract the phase modulation amplitude from the measured atomic population fractions as

$$\cot^2 \phi_a = \frac{n_0}{n_2}. \quad (3.65)$$

Here we note that the atomic phase can be evaluated at the antinodes of the lattice as

$\phi_a = \frac{\theta}{2} = \frac{\Omega_a t}{2}$, since $\cot \phi_a = \cot \frac{\theta}{2}$ follows from Eq. (3.64).

For molecules, we expand Eq. (3.61) as

$$\begin{aligned} \sqrt{\rho_m(x)}(\cos \phi_m + i \sin \phi_m) &= A_m \left(\gamma \cos^2\left(\frac{\theta}{2}\right) - i\gamma_2 \sin \theta e^{2ik_L x} - \gamma \sin^2\left(\frac{\theta}{2}\right) e^{4ik_L x} \right) \\ &= A_m \gamma \cos^2\left(\frac{\theta}{2}\right) - iA_m \gamma_2 \sin \theta (\cos 2k_L x + i \sin 2k_L x) \\ &\quad - A_m \gamma \sin^2\left(\frac{\theta}{2}\right) (\cos 4k_L x + i \sin 4k_L x). \end{aligned} \quad (3.66)$$

Organizing Eq. (3.66) into real and imaginary parts, dividing $\cos \phi_m$ by $\sin \phi_m$ gives us

$$\cot \phi_m = \frac{\cos \phi_m}{\sin \phi_m} = \frac{A_m \gamma \cos^2\left(\frac{\theta}{2}\right) + A_m \gamma_2 \sin \theta \sin 2k_L x - A_m \gamma \sin^2\left(\frac{\theta}{2}\right) \cos 4k_L x}{-A_m \gamma_2 \sin \theta \cos 2k_L x - A_m \gamma \sin^2\left(\frac{\theta}{2}\right) \sin 4k_L x} \quad (3.67)$$

Thus, we can evaluate the phase modulation amplitude on the molecules at $x = \lambda/4$ as

$$\cot \phi_m = \frac{\sqrt{m_0} - \sqrt{m_4}}{\sqrt{m_2}}, \quad (3.68)$$

where we have used $\sqrt{m_0} = A_m \gamma \cos^2 \frac{\theta}{2}$, $\sqrt{m_2} = A_m \gamma_2 \sin \theta$ and $\sqrt{m_4} = A_m \gamma \sin^2 \frac{\theta}{2}$.

We compare the molecular phase modulation amplitude $\phi_m \equiv \varphi_m(x = \lambda/4)$ to the atomic phase modulation amplitude ϕ_a obtained from Eqs. (3.65) and (3.68), see Fig. 3.4. The molecular phase evolves twice as much as the atomic phase, $\phi_m = 2\phi_a$, over several Rabi cycles, thereby confirming the occurrence of phase doubling during molecular synthesis.

A closer examination suggests a small nonlinear correction to the exact phase-doubling relation. The correction comes from the imbalance of the SFG and SHG coupling strengths $\gamma_2 \neq \gamma$. Substituting $\sqrt{m_0} = A_m \gamma \cos^2 \frac{\theta}{2}$, $\sqrt{m_2} = A_m \gamma_2 \sin \theta$ and $\sqrt{m_4} = A_m \gamma \sin^2 \frac{\theta}{2}$, we can rewrite Eq. (3.68) as

$$\phi_m = \cot^{-1} \left(\frac{\sqrt{m_0} - \sqrt{m_4}}{\sqrt{m_2}} \right) = \cot^{-1} \left(\frac{\gamma}{\gamma_2} \cot \theta \right). \quad (3.69)$$

Substituting $\gamma_2/\gamma = 1 - 2\epsilon$ into Eq. (3.69) and expanding the equation in terms of ϵ to leading order, we obtain

$$\begin{aligned} \phi_m &= \cot^{-1} \left(\frac{\gamma}{\gamma_2} \cot \theta \right) = \cot^{-1} \left(\frac{1}{1 - 2\epsilon} \cot \theta \right) \\ &= \theta - \epsilon \sin 2\theta + \mathcal{O}(\epsilon^2) = 2\phi_a - \epsilon \sin 4\phi_a + \mathcal{O}(\epsilon^2), \end{aligned} \quad (3.70)$$

from which we obtain $\epsilon = 0.06(2)$ from the fit to the data in Fig. 3.4, which is in agreement with the predicted value of $\epsilon = \frac{1}{2}(1 - \gamma_2/\gamma) \approx 0.09(2)$ from $\gamma_2/\gamma = 0.82(3)$. Here, we used $\phi_a = \Omega_a t/2 = \theta/2$. Eq. (3.70) also shows that exact phase doubling, $\phi_m = 2\phi_a$, occurs when $\gamma_2 = \gamma$, for which $\epsilon = \frac{1}{2}(1 - \gamma_2/\gamma) = 0$. When determining the phase beyond the first quadrant ($0 \leq \phi_a < \pi/2$) for Fig. 3.4, we use $\phi_a = \Omega_a t/2$ as a guide to determine the sign of

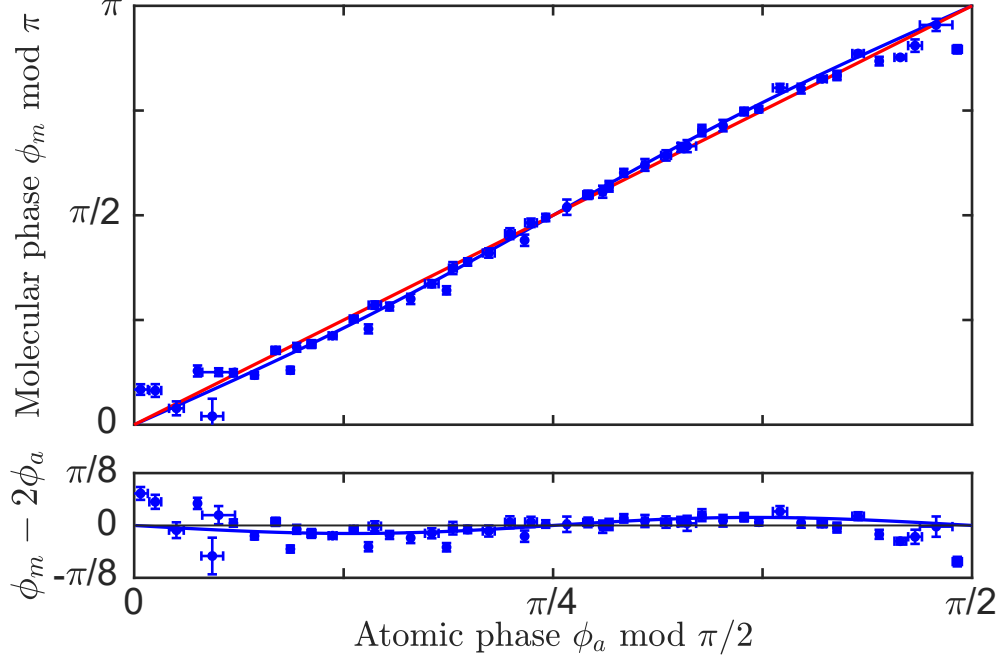


Figure 3.4: **Matter-wave phase doubling.** Phase relationship between the molecular phase ϕ_m and the atomic phase ϕ_a . The phases ϕ_a and ϕ_m are extracted from the diffraction patterns shown in Fig. 3.3. The measurements (blue circles) are compared to the red line which represents a linear ratio of $\phi_m/\phi_a = 2$. The blue line is the fit to the theoretical model $\phi_m = 2\phi_a - \epsilon \sin 4\phi_a$. The lower panel shows the deviation of the data from the phase doubling ratio $\phi_m = 2\phi_a$. The residual is fit with $-\epsilon \sin 4\phi_a$ (blue line), from which we obtain $\epsilon = 0.06(2)$.

$\cot \phi_a$ in other quadrants and flip the sign of the cotangent function accordingly. The correct phase in the second quadrant ($\pi/2 \leq \phi_a < \pi$) is given by $\phi_a = -\cot^{-1} \sqrt{n_0/n_2} + \pi$. Due to π -periodicity of the cotangent, the third quadrant has the same phase as the first and the fourth has the same as the second. This operation can be summarized in a single formula as $\phi_a \bmod \pi = (\cot^{-1} \sqrt{n_0/n_2} - \pi/2) \text{sgn}(\sin \Omega_a t) + \pi/2$, where the function $\text{sgn}(x) = 1$ for $x > 0$, 0 for $x = 0$ and -1 for $x < 0$. We perform a similar operation to get the molecular phase $\phi_m \bmod \pi$.

Additionally, there is a 1% offset between the measured atomic and molecular Rabi frequencies due to the systematic drift of the lattice beam intensity in the experiment. To compensate for this systematic effect, we apply a correction factor $\alpha = (\Omega_0 + \Omega_4)/2\Omega_a = 0.987$

to the atomic phase ϕ_a based on the measured Rabi frequencies of the molecules and atoms.

Our determination of both the atomic and molecular phase, ϕ_a and ϕ_m , is sensitive to the variation of the background, which shows a larger systematic uncertainty of the molecular phase near $\phi_a = 0$ and $\pi/2$.

To summarize our results, we imprint a periodic phase on the atomic BEC using a moving optical lattice. We then evaluate the phase-modulation amplitudes at the antinodes of the lattice. Using Eqs. (3.65) and (3.68), we extract the atomic and molecular phase-modulation amplitudes directly from their diffracted momentum-state populations. By taking the ratio ϕ_m/ϕ_a as a function of the pulse duration t , we show that the molecular phase evolves at twice the atomic phase, thereby confirming our expectation of matter-wave phase doubling. This process is analogous to phase matching in second harmonic generation; the phase matching condition is $k_{2\omega_1} = 2k_{\omega_1}$ which ensures that the generated field remains in phase with the driving polarization.

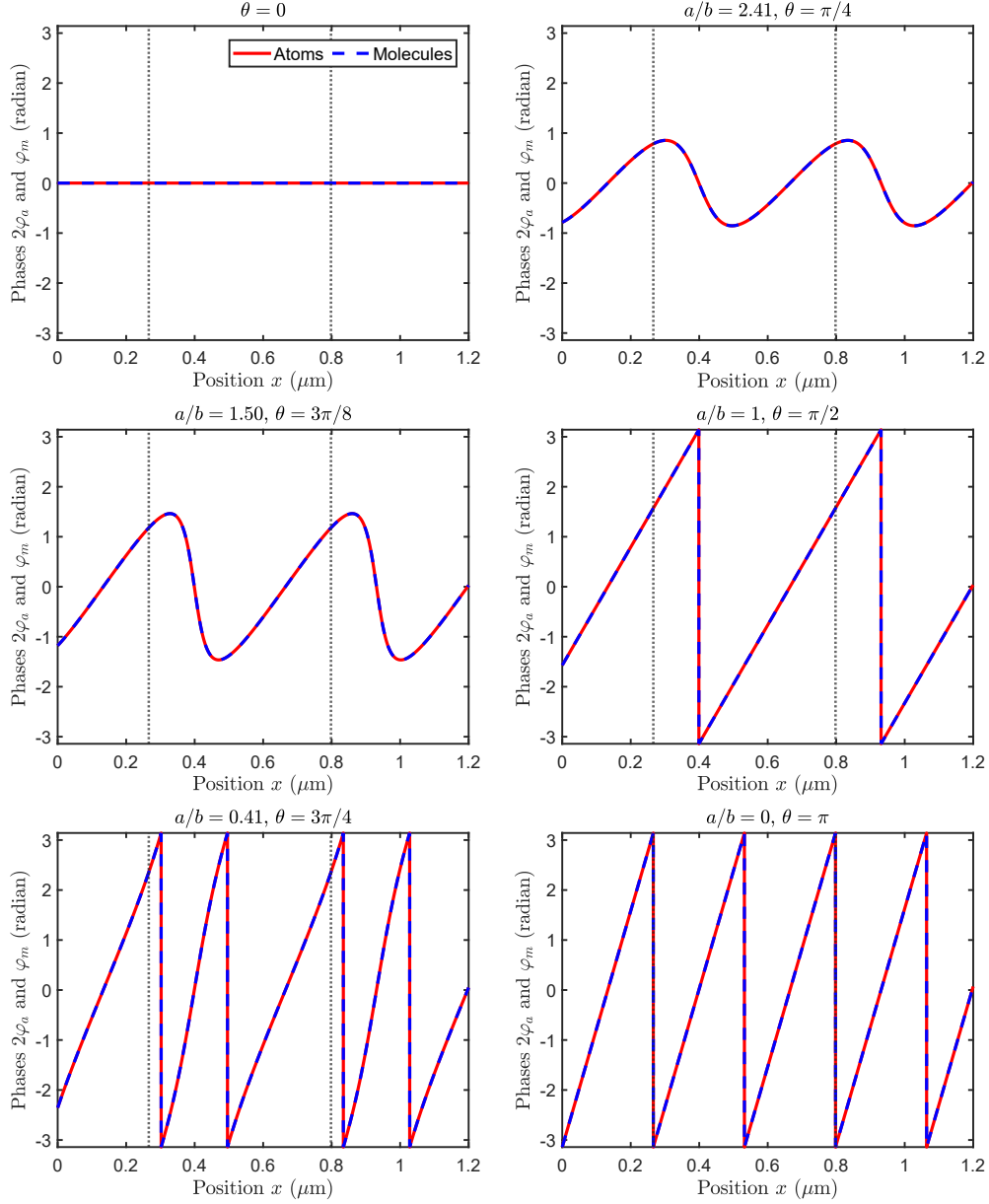


Figure 3.5: **Spatial dependence of phase modulation on atomic and molecular BECs.** The phases $2\varphi_a$ and φ_m are plotted as functions of position x for different values of the Bloch vector polar angle θ with $\gamma_2 = \gamma$. Vertical black dashed lines mark the intensity maxima of the optical lattice. The molecular phase is twice the atomic phase, $\varphi_m = 2\varphi_a$, at all positions of x . We compare the coefficients of the atomic wavefunction with $a/b = \cos(\theta/2)/\sin(\theta/2)$ for different values of θ .

CHAPTER 4

ENTANGLEMENT GENERATION

4.1 Breakdown of binomial statistics from molecular pairing

The molecular population fractions from Eqs. (3.32)–(3.34) yield $m_0 : m_2 : m_4 = 1 : 2 : 1$ at $\theta = \pi/2 \pmod{2\pi}$ pulses. This is consistent with the classical joint probability distribution $P(A, B)$ for flipping two coins, where $P(A, B) = P(A)P(B)$. Here, $P(A)$ denotes the marginal probability for the outcome of flipping coin A and likewise $P(B)$ for flipping coin B . Table 4.1 shows all possible outcomes for flipping two coins.

Table 4.1: **Classical joint probabilities for two uncorrelated coins.**

	$P(A)$	$P(B)$	$P(A, B) = P(A)P(B)$
$(A, B) = (\text{heads}, \text{heads})$	1/2	1/2	1/4
$(A, B) = (\text{heads}, \text{tails})$	1/2	1/2	1/4
$(A, B) = (\text{tails}, \text{heads})$	1/2	1/2	1/4
$(A, B) = (\text{tails}, \text{tails})$	1/2	1/2	1/4

By tallying the outcomes corresponding to two heads, one head, or no heads, we obtain the characteristic ratio of $1 : 2 : 1$, in agreement with the predictions of Eqs. (3.32)–(3.34) where the addition of momenta plays the role of heads and tails.

However, we obtain molecular population ratios of $m_0 : m_2 : m_4 = 0.21(1) : 0.58(1) : 0.21(1)$ after a $\pi/2$ Bragg pulse on the atoms from the data in Fig. 3.3. Furthermore, Eqns. (3.32)–(3.34) in our theory model suggest a molecular population ratio of $m_0 : m_2 : m_4 = 1 : 4 : 1$, assuming atoms are prepared in an equal superposition of $|0\rangle$ and $|2k_L\rangle$ and the coupling strengths are equal, $\gamma_2 = \gamma$. These results indicate that the molecular

wavefunction can not be expressed as a simple product state of two atomic wavefunctions, $\psi_m \neq \psi_a \otimes \psi_a$, since such a separable state would yield statistically independent measurement outcomes and hence binomial counting statistics.

4.2 Two-spin parity measurement

To assess the non-separability of the molecular state in a more rigorous manner, we introduce the spin parity operator. Let us consider a system of N spins with angular momenta $\mathbf{S}_j = \frac{\hbar}{2} \boldsymbol{\sigma}_j$ for the j -th spin, where $\boldsymbol{\sigma}$ is the Pauli vector. We define the spin coherence operators as $\hat{C}_{\mu\mu} = \prod_j^N \sigma_{j,\mu}$, where $\mu = x, y$ and z .

In a system with $N = 2$ spins, we define the wavefunction as a product state, $|\psi\rangle = |1\rangle \otimes |2\rangle$. In addition, we define the Bloch vectors as $\mathbf{b}_j = \langle j | \boldsymbol{\sigma}_j | j \rangle = (b_{j,x}, b_{j,y}, b_{j,z})$, where $j=1, 2$ refers to the spins and $|\mathbf{b}_j| = 1$. We define the sum of the spin coherence operators as $\hat{S} = \sum_{\mu=x,y,z} \left(\prod_j^N \sigma_{j,\mu} \right)$. Taking the expectation value of $\hat{S}$ gives us

$$\begin{aligned}
\langle \hat{S} \rangle &= \sum_{\mu=x,y,z} \langle \sigma_{1,\mu} \otimes \sigma_{2,\mu} \rangle = \langle \sigma_{1,x} \otimes \sigma_{2,x} \rangle + \langle \sigma_{1,y} \otimes \sigma_{2,y} \rangle + \langle \sigma_{1,z} \otimes \sigma_{2,z} \rangle \\
&= (\langle 1 | \otimes \langle 2 |) (\sigma_{1,x} |1\rangle \otimes \sigma_{2,x} |2\rangle) + (\langle 1 | \otimes \langle 2 |) (\sigma_{1,y} |1\rangle \otimes \sigma_{2,y} |2\rangle) + (\langle 1 | \otimes \langle 2 |) (\sigma_{1,z} |1\rangle \otimes \sigma_{2,z} |2\rangle) \\
&= \langle 1 | \sigma_{1,x} | 1 \rangle \langle 2 | \sigma_{2,x} | 2 \rangle + \langle 1 | \sigma_{1,y} | 1 \rangle \langle 2 | \sigma_{2,y} | 2 \rangle + \langle 1 | \sigma_{1,z} | 1 \rangle \langle 2 | \sigma_{2,z} | 2 \rangle \\
&= b_{1,x} b_{2,x} + b_{1,y} b_{2,y} + b_{1,z} b_{2,z} = \mathbf{b}_1 \cdot \mathbf{b}_2
\end{aligned} \tag{4.1}$$

Applying the Cauchy-Schwarz inequality to $\langle \hat{S} \rangle$, we can establish the upper bound for $|\langle \hat{S} \rangle|$,

$$|\langle \hat{S} \rangle| = |\mathbf{b}_1 \cdot \mathbf{b}_2| \leq |\mathbf{b}_1| |\mathbf{b}_2| = 1. \tag{4.2}$$

Since the molecular state is a product state of atoms with identical Bloch vectors, $\mathbf{b}_1 = \mathbf{b}_2 = (b_x, b_y, b_z)$, the expectation value of the spin-parity operator, $C_{zz} = \langle \hat{C}_{zz} \rangle = \langle \psi | \sigma_{1,z} \sigma_{2,z} | \psi \rangle =$

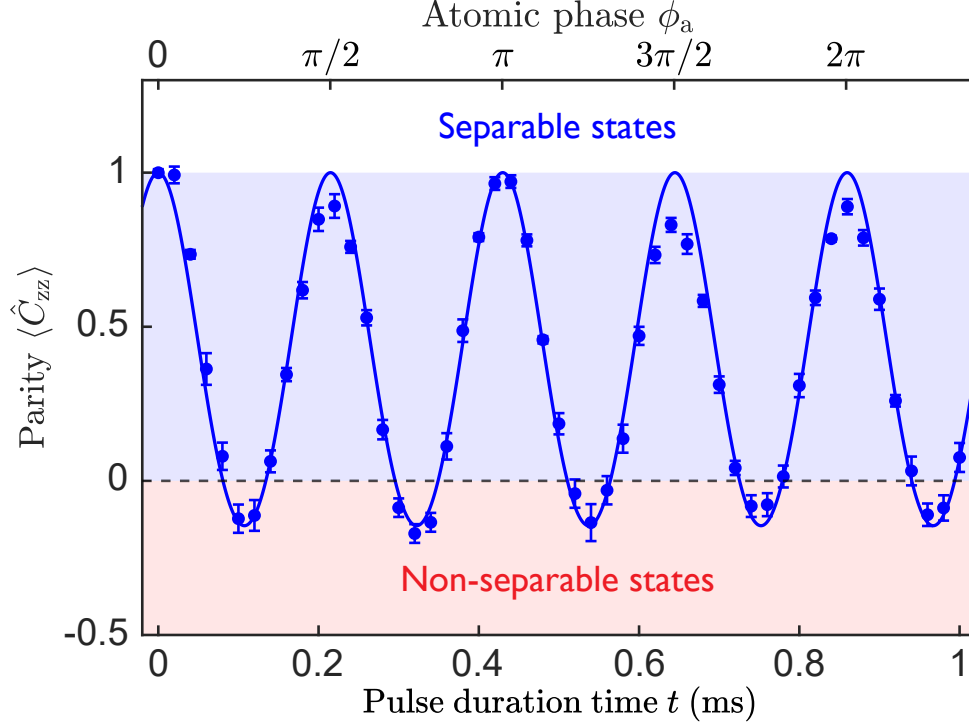


Figure 4.1: **Two-spin parity measurement of the molecular state.** Parity is defined as $\langle \hat{C}_{zz} \rangle = m_0 - m_2 + m_4$ for molecules. Negative values of parity $-1 \leq \langle \hat{C}_{zz} \rangle < 0$ indicate non-separability of the two-atom momentum state. The parity reaches its minimum of $\langle \hat{C}_{zz} \rangle = -0.15$ after applying $\theta = 2\phi_a \equiv \pi/2 \pmod{2\pi}$ Bragg pulses on the atoms. Error bars show 1- σ standard deviation of the mean of five measurements.

b_z^2 , is constrained from below as

$$\begin{aligned} 0 \leq b_z^2 \leq b_x^2 + b_y^2 + b_z^2 = 1, \\ \Rightarrow 0 \leq C_{zz} \leq 1. \end{aligned} \tag{4.3}$$

Therefore, any negative value of C_{zz} indicates that the molecular wavefunction cannot be written as a product state of two identical atomic wavefunctions. In our experiment, the measured parity spans $-0.15 \lesssim C_{zz} < 1$, thus demonstrating the molecular state is non-separable with respect to its atomic constituents. Fig. 4.1 shows that C_{zz} reaches its minimum when atoms are prepared in an equal superposition of $|0\rangle$ and $|2k_L\rangle$ after $\pi/2$, $3\pi/2$, ... Bragg pulses.

While the term "parity operator" frequently appears in the context of quantum information science (QIS), it plays a different role in our system. In QIS, especially in trapped-ion experiments, parity oscillations of Greenberger–Horne–Zeilinger (GHZ)-type states are used to demonstrate N -body spin coherence, GHZ-state fidelity and Heisenberg-limited phase sensitivity [35, 36, 37]. In contrast to trapped-ion experiments, we use the same parity operator as a model-restricted entanglement witness to test the non-separability of the molecular state rather than GHZ-type coherence.

4.3 Peres-Horodecki criterion and Bell state entanglement witnesses

While the parity operator signals the generation of non-separable molecular states after $\pi/2$, $3\pi/2$, ... Bragg pulses, it does not specify the nature of the entanglement. To elucidate the nature of this entanglement, we adopt more conventional diagnostics.

Bell inequalities are among the most well-known examples of entanglement witnesses. Separable states do not violate any Bell inequality. However, the assumption that all entangled states must violate a Bell inequality is incorrect. Some entangled states admit a local hidden variable (LHV) model and thus do not violate Bell inequalities. Therefore, Bell inequalities are regarded as *non-optimal* entanglement witnesses, detecting only a restricted class of entangled states. The relation between separable and non-separable states, as well as the relation between LHV and non-LHV states is illustrated in Fig. 4.2.

To address this issue, one can construct *optimal* entanglement witnesses, capable of distinguishing between separable and non-separable states, based on the Peres–Horodecki criterion [39, 40]. The Peres-Horodecki criterion, also known as the positive partial transpose (PPT) criterion, states that a bipartite density matrix ϱ is entangled if and only if its partial transpose has at least one negative eigenvalue. Conversely, PPT states are those whose partial transpose has only non-negative eigenvalues. This criterion is necessary and sufficient

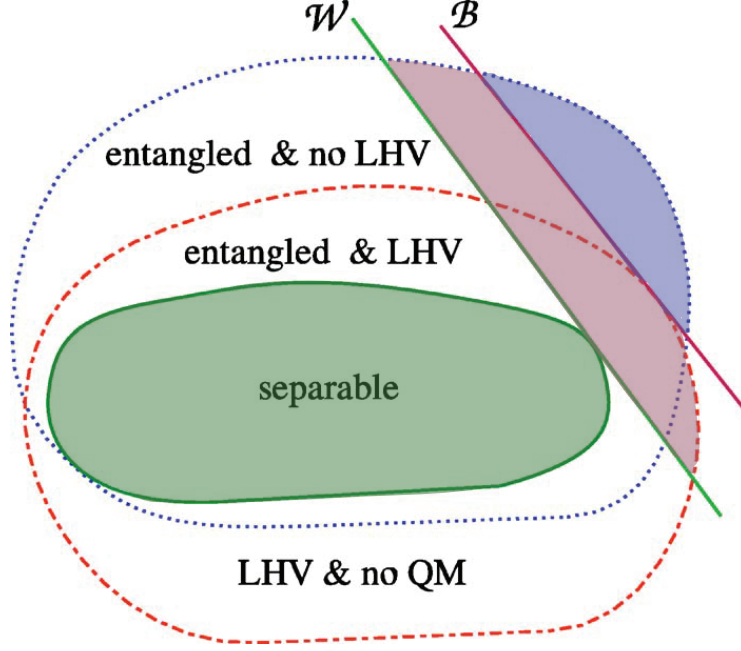


Figure 4.2: **Schematic of different types of correlations.** Correlations can arise from four distinct states: entangled states that do not admit a local hidden variable (LHV) model (blue shaded region), entangled states that admit a LHV model (red shaded region), separable states (green shaded region), and classical LHV models. Bell inequalities $\mathcal{B}$ (solid red line) do not differentiate between entangled states that admit a LHV model and separable states. Entanglement witnesses $\mathcal{W}$ (solid green line) are constructed to distinguish between non-separable and separable states. Figure adapted from Hyllus et al. [38].

for testing separability in 2×2 and 2×3 dimensional Hilbert spaces. At higher dimensions, it becomes insufficient because PPT-entangled states also have positive partial-transpose eigenvalues.

If a bipartite state violates the Peres-Horodecki criterion, there exists an entanglement witness that detects that specific state. An entanglement witness $\hat{W}$ is a Hermitian operator that satisfies $\text{Tr} [\hat{W} \rho] \geq 0$ for all separable states and $\text{Tr} [\hat{W} \rho] < 0$ for the target entangled state. The *optimal* entanglement witness is defined as $\hat{W} = |\varrho_e\rangle \langle \varrho_e|^{T_A}$ where $|\varrho_e\rangle$ is the eigenvector that corresponds to the negative eigenvalue of ρ^{T_A} [41, 38]. Here T_A refers to the partial transpose of the first subsystem.

Using this definition of $\hat{W}$, we can determine the entanglement witnesses corresponding to the Bell states $|\Phi^\pm\rangle = (|0, 0\rangle \pm |1, 1\rangle)/\sqrt{2}$ and $|\Psi^\pm\rangle = (|0, 1\rangle \pm |1, 0\rangle)/\sqrt{2}$, where the basis

kets are defined as $|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Here we demonstrate how to construct the entanglement witness associated with the Bell state $|\Phi^+\rangle = (|0,0\rangle + |1,1\rangle)/\sqrt{2}$.

The density matrices for all four Bell states are expressed as

$$\begin{aligned} \varrho_{\Phi^+} &= |\Phi^+\rangle \langle \Phi^+| = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix}, & \varrho_{\Phi^-} &= |\Phi^-\rangle \langle \Phi^-| = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 \end{pmatrix}, \\ \varrho_{\Psi^+} &= |\Psi^+\rangle \langle \Psi^+| = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, & \varrho_{\Psi^-} &= |\Psi^-\rangle \langle \Psi^-| = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \end{aligned}$$

By transposing the first subsystem, the partial transpose of ϱ_{Φ^+} is

$$\varrho_{\Phi^+}^{TA} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (4.4)$$

The eigenvalues of $\varrho_{\Phi^+}^{TA}$ are $1/2, 1/2, 1/2, -1/2$, thus the partial transpose has a negative eigenvalue which violates the Peres-Horodecki criterion. We now determine the eigenvector associated with the negative eigenvalue. By evaluating the expectation values of $\varrho_{\Phi^+}^{TA}$ in the Bell state basis, we obtain $\text{Tr}(\varrho_{\Phi^+}^{TA} \varrho_{\Phi^+}) = \text{Tr}(\varrho_{\Phi^+}^{TA} \varrho_{\Phi^-}) = \text{Tr}(\varrho_{\Phi^+}^{TA} \varrho_{\Psi^+}) = 1/2$ and $\text{Tr}(\varrho_{\Phi^+}^{TA} \varrho_{\Psi^-}) = -1/2$ which shows that $|\Psi^-\rangle$ is the eigenvector associated with the negative eigenvalue. Thus, the *optimal* witness associated with the Bell state $|\Phi^+\rangle$ is $(|\Psi^-\rangle \langle \Psi^-|)^{TA}$.

We redefine the entanglement witness for $|\Phi^+\rangle$ as $\hat{W}_{\Phi^+} = \Gamma(|\Psi^-\rangle \langle \Psi^-|)^{TA}$ where the partial transpose of $|\Psi^-\rangle \langle \Psi^-|$ has been rescaled by a factor of $\Gamma = -4$. Rewriting $\hat{W}_{\Phi^+}$ in terms of the spin coherence operators, $\hat{C}_{xx} = \sigma_x \otimes \sigma_x$, $\hat{C}_{yy} = \sigma_y \otimes \sigma_y$ and $\hat{C}_{zz} = \sigma_z \otimes \sigma_z$, we obtain $\hat{W}_{\Phi^+} = \hat{C}_{xx} - \hat{C}_{yy} + \hat{C}_{zz} - \hat{I}$. By evaluating the expectation values of $\hat{W}_{\Phi^+}$ in

Table 4.2: **Bell state witnesses for different two-spin states.** Entanglement witnesses are constructed to detect a specific Bell state, thus yielding negative expectation values for all other Bell states. A positive expectation value of the witness indicates correlations aligned with that particular Bell state. Witnesses evaluated at $\phi_a = \pi/4$ show that only $W_{\Psi+}$ has a positive value, while $W_{\Phi+}$ and $W_{\Psi-}$ are completely insensitive with values of -2 , corresponding to the lower bound for separable states. The last column shows the expected witnesses at $\phi_a = \pi/4$ for the ideal case in which the Feshbach couplings for sum frequency and second harmonic generation are equal.

	$ \Phi^+\rangle$	$ \Phi^-\rangle$	$ \Psi^+\rangle$	$ \Psi^-\rangle$	product	Exp. data at	$\gamma_2 = \gamma$
	$\frac{ 00\rangle+ 11\rangle}{\sqrt{2}}$	$\frac{ 00\rangle- 11\rangle}{\sqrt{2}}$	$\frac{ 01\rangle+ 10\rangle}{\sqrt{2}}$	$\frac{ 01\rangle- 10\rangle}{\sqrt{2}}$	state	$\phi_a = \pi/4$	
$W_{\Phi+}$	2	-2	-2	-2	≤ 0	-2.0(1)	-2
$W_{\Phi-}$	-2	2	-2	-2	≤ 0	-0.23(2)	-2/3
$W_{\Psi+}$	-2	-2	2	-2	≤ 0	0.29(2)	2/3
$W_{\Psi-}$	-2	-2	-2	2	≤ 0	-2.00(2)	-2

the Bell state basis, we obtain $\text{Tr}(\hat{W}_{\Phi+}\varrho_{\Phi+}) = 2$ and $\text{Tr}(\hat{W}_{\Phi+}\varrho_{\Phi-}) = \text{Tr}(\hat{W}_{\Phi+}\varrho_{\Psi+}) = \text{Tr}(\hat{W}_{\Phi+}\varrho_{\Psi-}) = -2$ which shows that the witness $\hat{W}_{\Phi+}$ detects only the Bell state $|\Phi^+\rangle$.

The signs of the expectation values are reversed due to the rescaling factor.

The entanglement witnesses for the remaining Bell states can be constructed in the same manner. Thus, the witnesses take the form

$$\hat{W}_{\Phi+} = -4(|\Psi^-\rangle \langle \Psi^-|)^{TA} = \hat{C}_{xx} - \hat{C}_{yy} + \hat{C}_{zz} - \hat{I}, \quad (4.5)$$

$$\hat{W}_{\Phi-} = -4(|\Psi^+\rangle \langle \Psi^+|)^{TA} = -\hat{C}_{xx} + \hat{C}_{yy} + \hat{C}_{zz} - \hat{I}, \quad (4.6)$$

$$\hat{W}_{\Psi+} = -4(|\Phi^-\rangle \langle \Phi^-|)^{TA} = \hat{C}_{xx} + \hat{C}_{yy} - \hat{C}_{zz} - \hat{I}. \quad (4.7)$$

$$\hat{W}_{\Psi-} = -4(|\Phi^+\rangle \langle \Phi^+|)^{TA} = -\hat{C}_{xx} - \hat{C}_{yy} - \hat{C}_{zz} - \hat{I}. \quad (4.8)$$

Table 4.2 summarizes the expectation values of $\hat{W}_{\Phi\pm}$ and $\hat{W}_{\Psi\pm}$ in the Bell state basis.

To evaluate these witness operators in the molecular basis, $|0\rangle_s$, $|2k_L\rangle_s$, and $|4k_L\rangle_s$, we first apply a similarity transformation to the operators $\sigma_x^{\otimes 2}$, $\sigma_y^{\otimes 2}$ and $\sigma_z^{\otimes 2}$ using the transformation operator $\hat{U}_1$, which maps the two-qubit Hilbert space onto the spin-1 manifold, yielding the transformed operators

$$\begin{aligned}\hat{C}_{xx} &= \hat{U}_1 \sigma_x^{\otimes 2} \hat{U}_1^\dagger = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \hat{C}_{yy} = \hat{U}_1 \sigma_y^{\otimes 2} \hat{U}_1^\dagger = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \\ \hat{C}_{zz} &= \hat{U}_1 \sigma_z^{\otimes 2} \hat{U}_1^\dagger = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.\end{aligned}$$

Setting the molecular wavefunction as $|\psi_m\rangle = \sqrt{m_0}|0\rangle_s - i\sqrt{m_2}|2k_L\rangle_s - \sqrt{m_4}|4k_L\rangle_s$, we can evaluate the expectation values of the spin coherence operators as

$$C_{xx} = \langle \hat{C}_{xx} \rangle = \langle \psi_m | \hat{C}_{xx} | \psi_m \rangle = m_2 - 2\sqrt{m_0 m_4}, \quad (4.9)$$

$$C_{yy} = \langle \hat{C}_{yy} \rangle = \langle \psi_m | \hat{C}_{yy} | \psi_m \rangle = m_2 + 2\sqrt{m_0 m_4}, \quad (4.10)$$

$$C_{zz} = \langle \hat{C}_{zz} \rangle = \langle \psi_m | \hat{C}_{zz} | \psi_m \rangle = m_0 - m_2 + m_4. \quad (4.11)$$

Thus, the expectation values of the witness operators are

$$W_{\Phi+} = C_{xx} - C_{yy} + C_{zz} - 1 = m_0 - m_2 + m_4 - 4\sqrt{m_0 m_4} - 1, \quad (4.12)$$

$$W_{\Phi-} = -C_{xx} + C_{yy} + C_{zz} - 1 = m_0 - m_2 + m_4 + 4\sqrt{m_0 m_4} - 1, \quad (4.13)$$

$$W_{\Psi+} = C_{xx} - C_{yy} - C_{zz} - 1 = 3m_2 - m_0 - m_4 - 1 = -2C_{zz}, \quad (4.14)$$

$$W_{\Psi-} = -C_{xx} - C_{yy} - C_{zz} - 1 = -m_0 - m_2 - m_4 - 1 = -2. \quad (4.15)$$

The witnesses give positive values $W_{\Phi\pm}, W_{\Psi\pm} > 0$ for non-separable states. On the other hand, the witnesses give non-positive values $W_{\Phi\pm}, W_{\Psi\pm} \leq 0$ for product states. Each witness

is sensitive only to the entangled state it was constructed to detect. For example, a positive value of W_{Φ^+} indicates that the state exhibits correlations characteristic of the Bell state $|\Phi^+\rangle$, even if the state itself is not maximally entangled.

We can now apply these witnesses to our measurements. In our experiment, the momentum state $|k=0\rangle$ maps to $|0\rangle$, while $|k=2k_L\rangle$ maps to $|1\rangle$. After applying a $\pi/2$ Bragg pulse on the atoms, we measure molecular population fractions of $m_2 = 0.58(1)$ and $m_0 = m_4 = 0.21(1)$. From fitting the witnesses $W_{\Phi^\pm}$ and $W_{\Psi^\pm}$ with Eqs. (3.58), (3.59) and (3.60) with coupling strength ratio γ_2/γ and Rabi frequency Ω_a as free parameters, we obtain $W_{\Psi^+} = 0.29(2) > 0$ at $\phi_a = \pi/4, 3\pi/4, \dots$, which suggests the molecular state is not separable and is more aligned with $|\Psi^+\rangle$ compared to other states with lower values of $W_{\Psi^-} = -2$, $W_{\Phi^+} = -2$ and $W_{\Phi^-} = -0.23(2)$. For a $\pi/2$ -pulse, the witness W_{Ψ^+} can be expressed in terms of γ_2/γ as

$$W_{\Psi^+}(\phi_a = \pi/4) = \frac{2(\gamma_2/\gamma)^2 - 1}{(\gamma_2/\gamma)^2 + 1/2}. \quad (4.16)$$

When the coupling strengths are equal, $\gamma_2 = \gamma$, we obtain a maximum of $W_{\Psi^+} = 2/3$.

To characterize non-classical correlations in the molecular momentum state, it is instructive to express the molecular momentum wavefunction in the Bell state basis. By applying the transformation operator $\hat{U}_1$ to the Bell states, we obtain

$$\begin{aligned} |\tilde{\Phi}^+\rangle &= \hat{U}_1 |\Phi^+\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{pmatrix}, & |\tilde{\Phi}^-\rangle &= \hat{U}_1 |\Phi^-\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \\ |\tilde{\Psi}^+\rangle &= \hat{U}_1 |\Psi^+\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, & |\tilde{\Psi}^-\rangle &= \hat{U}_1 |\Psi^-\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}. \end{aligned}$$

Thus, the transformation operator $\hat{U}_1$ selects the symmetric triplet subspace $(|\Phi^+\rangle, |\Phi^-\rangle,$

$|\Psi^+\rangle\rangle$ while annihilating the antisymmetric singlet state $|\Psi^-\rangle$. Using the new Bell state basis, we can express the molecular wavefunction at $\phi_a = \pi/4 \pmod{\pi/2}$ as

$$\begin{aligned}
|\psi_m(\phi_a = \pi/4)\rangle &= \sqrt{m_0}|0\rangle_s - i\sqrt{m_2}|2k_L\rangle_s - \sqrt{m_4}|4k_L\rangle_s \\
&= \begin{pmatrix} \sqrt{m_0} \\ -i\sqrt{m_2} \\ -\sqrt{m_4} \end{pmatrix} = \sqrt{m_0} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} - i\sqrt{m_2} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \\
&= \frac{1}{2} \frac{1}{\left(\left(\frac{\gamma_2}{\gamma}\right)^2 + \frac{1}{2}\right)^{1/2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} - i \frac{\frac{\gamma_2}{\gamma}}{\left(\left(\frac{\gamma_2}{\gamma}\right)^2 + \frac{1}{2}\right)^{1/2}} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad (4.17) \\
&= \frac{1}{2} \sqrt{2 - W_{\Psi^+}} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ -\frac{1}{\sqrt{2}} \end{pmatrix} - \frac{i}{2} \sqrt{2 + W_{\Psi^+}} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \\
&= \frac{1}{2} \sqrt{2 - W_{\Psi^+}} |\tilde{\Phi}^-\rangle - \frac{i}{2} \sqrt{2 + W_{\Psi^+}} |\tilde{\Psi}^+\rangle.
\end{aligned}$$

From our measured value of $W_{\Psi^+} = 0.29(2)$, we obtain $|\langle \tilde{\Phi}^- | \psi_m(\phi_a = \pi/4) \rangle|^2 = 0.43(1)$ and $|\langle \tilde{\Psi}^+ | \psi_m(\phi_a = \pi/4) \rangle|^2 = 0.57(1)$. Thus, a positive value of W_{Ψ^+} signals the prevalence of correlations associated with the Bell state $|\Psi^+\rangle$, whereas a negative value indicates the prevalence of correlations associated with the complementary Bell state $|\Phi^-\rangle$.

Instead of entanglement witnesses, we can also evaluate the Bell state fidelities, which quantify the overlap of the molecular state with each maximally entangled Bell state. The fidelity is defined as $\mathcal{F} = \langle B | \varrho_m | B \rangle$ where ϱ is the molecular density matrix and $|B\rangle$ is a Bell state. The density matrix ϱ_m is

$$\varrho_m = |\psi_m\rangle \langle \psi_m| = \begin{pmatrix} m_0 & i\sqrt{m_0 m_2} & -\sqrt{m_0 m_4} \\ -i\sqrt{m_0 m_2} & m_2 & i\sqrt{m_2 m_4} \\ -\sqrt{m_0 m_4} & -i\sqrt{m_2 m_4} & m_4 \end{pmatrix}. \quad (4.18)$$

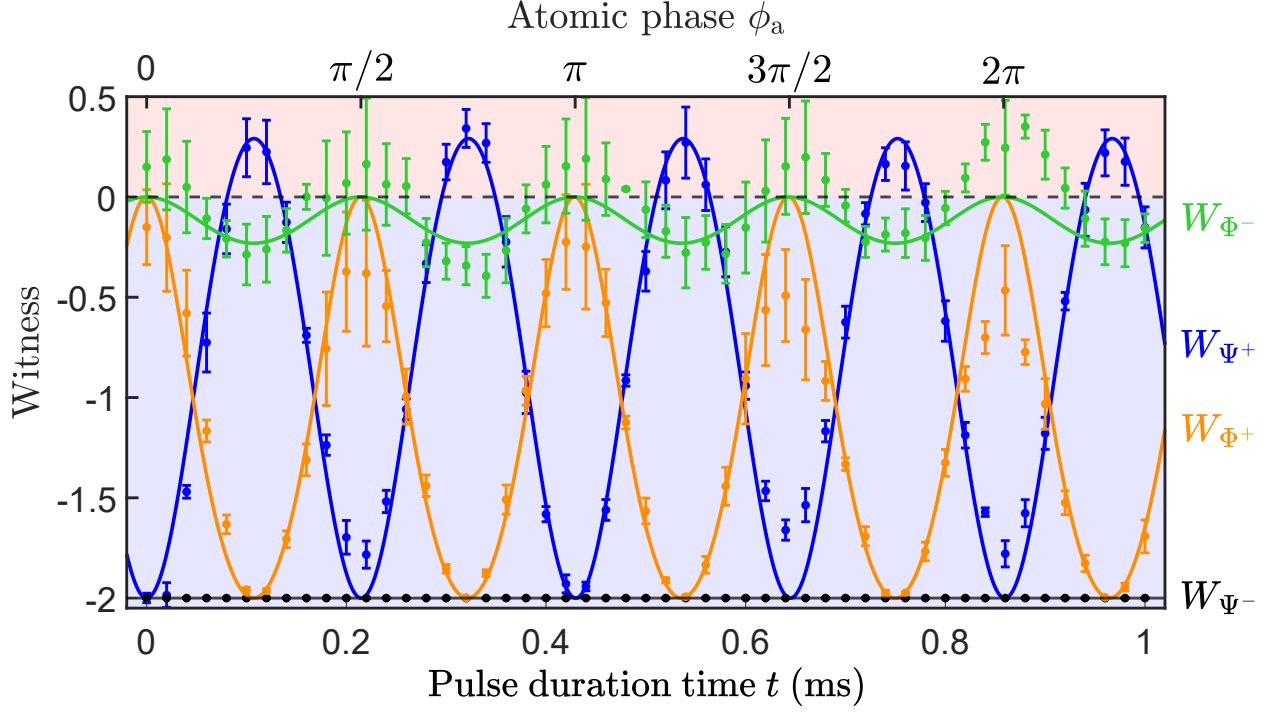


Figure 4.3: **Bell state entanglement witnesses.** The witnesses $W_{\Phi+}$ (orange), $W_{\Phi-}$ (green), $W_{\Psi+}$ (blue), and $W_{\Psi-}$ (black) are plotted as a function of pulse duration time t . The red and blue areas represent non-separable and separable states, respectively. $W_{\Psi+}$ exceeds the upper limit of zero at $\phi_a = \pi/4, 3\pi/4, 5\pi/4, 7\pi/4, \dots$, reaching a maximum of $W_{\Psi+} = 0.29(2)$ from the fit, thus indicating entanglement. $W_{\Phi-}$ appears to exceed zero at $\phi_a = 0, \pi/2, \pi, 3\pi/2, \dots$, due to large relative uncertainties of the populations close to zero in Eq. (4.13). Furthermore, the majority of atoms occupy a single momentum state (either $|0\rangle$ or $|2k_L\rangle$) at $\phi_a = 0, \pi/2, \pi, 3\pi/2, \dots$, and thus are unable to generate an entangled state.

Thus, the Bell state fidelities can be expressed in the following forms

$$\mathcal{F}_{\Phi+} = \langle \tilde{\Phi}^+ | \varrho_m | \tilde{\Phi}^+ \rangle = \frac{1}{2} (\sqrt{m_0} - \sqrt{m_4})^2 = \frac{1}{2} \frac{\cos^2 \theta}{1 + [(\gamma_2/\gamma)^2 - 1/2] \sin^2 \theta}, \quad (4.19)$$

$$\mathcal{F}_{\Phi-} = \langle \tilde{\Phi}^- | \varrho_m | \tilde{\Phi}^- \rangle = \frac{1}{2} (\sqrt{m_0} + \sqrt{m_4})^2 = \frac{1}{2} \frac{1}{1 + [(\gamma_2/\gamma)^2 - 1/2] \sin^2 \theta}, \quad (4.20)$$

$$\mathcal{F}_{\Psi+} = \langle \tilde{\Psi}^+ | \varrho_m | \tilde{\Psi}^+ \rangle = m_2 = \frac{(\gamma_2/\gamma)^2 \sin^2 \theta}{1 + [(\gamma_2/\gamma)^2 - 1/2] \sin^2 \theta}, \quad (4.21)$$

with the exception of $\mathcal{F}_{\Psi-} = \langle \tilde{\Psi}^- | \varrho_m | \tilde{\Psi}^- \rangle = 0$, where we have used the transformed Bell states restricted to the triplet subspace. The Bell state fidelities are bounded by $0 \leq \mathcal{F} \leq 1/2$

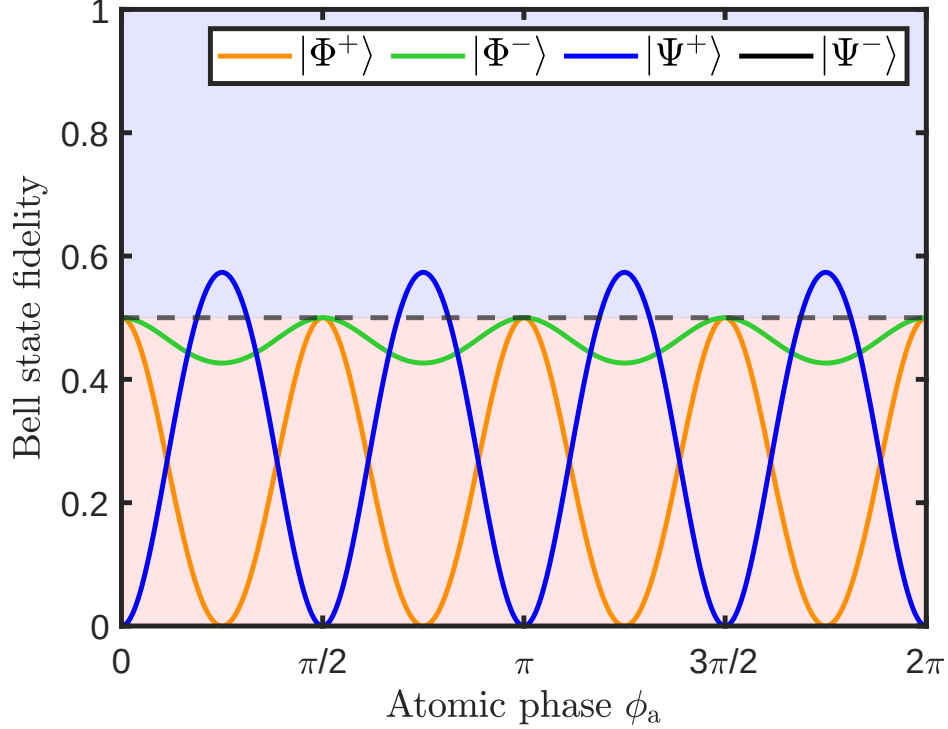


Figure 4.4: **Bell state fidelities $\mathcal{F}$.** Fidelities $\mathcal{F}_{\Phi^+}$, $\mathcal{F}_{\Phi^-}$, $\mathcal{F}_{\Psi^+}$, and $\mathcal{F}_{\Psi^-}$ are plotted as functions of the atomic phase ϕ_a , using fitting parameters extracted from the measurement. All separable states satisfy $\mathcal{F} \leq 1/2$ whereas entangled states must satisfy $\mathcal{F} > 1/2$. From our measurement results, $\mathcal{F}_{\Psi^+}$ exceeds $1/2$ at $\phi_a = \pi/4, 3\pi/4, \dots$ Bragg pulses.

for all separable states. In contrast, entangled states satisfy $1/2 < \mathcal{F} \leq 1$, with the Bell states reaching $\mathcal{F} = 1$. Fig. 4.4 shows that $\mathcal{F}_{\Psi^+}$ exceeds the upper bound of separable states at $\phi_a = \pi/4, 3\pi/4, \dots$ Bragg pulses, consistent with the results from Fig. 4.3.

4.4 Nonlinear wave mixing as a source of entanglement

The witnesses reveal signatures of non-classical correlations associated with the Bell state $|\Psi^+\rangle$ in the molecular wavefunction. However, it is worth noting that it is not individual molecules themselves that become momentum-entangled; rather, *pairs of atoms* become momentum-entangled during the reaction. The witnesses detect the non-classical momentum correlations generated during the reaction and subsequently encoded in the final molecular momentum wavefunction. In this section, we examine the source of this entanglement.

For sufficiently large detuning, we can safely ignore the molecular fields and model the effective reaction Hamiltonian as $\hat{H}_a \approx (\hat{a}_0 + \hat{a}_2)^2$, where $\hat{a}_j$ is the atomic field operator for the mode with momentum $2jk_L$ ($j \in \mathbb{N}$). In this reaction, the Hamiltonian mixes the atomic matter waves with different momenta. Expanding this Hamiltonian generates the symmetrized operator $\hat{a}_0\hat{a}_2 + \hat{a}_2\hat{a}_0$. Since the two reaction pathways are indistinguishable, their amplitudes add coherently, yielding $\hat{a}_0\hat{a}_2 + \hat{a}_2\hat{a}_0 = 2\hat{a}_2\hat{a}_0$. Thus the expectation value of the cross term yields $M_2 \propto 4 \langle \hat{a}_0^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_0 \rangle = 4 \langle a_0 | \hat{a}_0^\dagger \hat{a}_0 | a_0 \rangle \langle a_2 | \hat{a}_2^\dagger \hat{a}_2 | a_2 \rangle = 4N_0N_2$ which is twice the classical joint probability of $2 \langle \hat{a}_0^\dagger \hat{a}_0 \rangle \langle \hat{a}_2^\dagger \hat{a}_2 \rangle = 2N_0N_2$, where $N_0 = \langle \hat{a}_0^\dagger \hat{a}_0 \rangle$ and $N_2 = \langle \hat{a}_2^\dagger \hat{a}_2 \rangle$. To summarize, nonlinear wave mixing generates non-classical momentum correlations between atoms via the symmetrized pair-annihilation operator, and the indistinguishability of the two reaction pathways leads to coherent addition of their field amplitudes, thereby doubling the population of molecules with momentum $2k_L$ produced by the mixing process. The enhancement of M_2 , amounting to twice the classical expectation, is detected by the entanglement witness W_{Ψ^+} corresponding to the Bell state $|\Psi^+\rangle = (|k=0\rangle|2k_L\rangle + |2k_L\rangle|0\rangle)/\sqrt{2}$.

Nonlinear wave mixing can also generate strong non-classical correlations even in the absence of bosonic symmetrization. Here we consider the case in which the sum frequency coupling strength is much weaker than the second harmonic coupling strength. For example, when $\gamma_2/\gamma = 0.1$, we obtain $|\langle \tilde{\Phi}^- | \psi_m(\phi_a = \pi/4) \rangle|^2 = 0.98$ and $|\langle \tilde{\Psi}^+ | \psi_m(\phi_a = \pi/4) \rangle|^2 = 0.02$ from Eq. (4.17), where $W_{\Psi^+} \approx -1.92$. These results demonstrate that wave mixing induces correlations between atoms in the *same momentum state*, sufficiently strong enough for the molecular two-qubit wavefunction to align almost completely with the Bell state $|\Phi^-\rangle = (|k=0\rangle|k=0\rangle - |2k_L\rangle|2k_L\rangle)/\sqrt{2}$.

To conclude, reactions in the quantum degenerate regime are characterized as nonlinear wave mixing processes that induce non-classical correlations between reacting atoms. These correlations can be detected using entanglement witnesses based on the Peres-Horodecki criterion for 2×2 and 2×3 dimensional Hilbert spaces. In our experiment, the witnesses detect momentum correlations aligned with the Bell state $|\Psi^+\rangle$. In addition, the indistinguishability of the reaction pathways enables the coherent addition of the atomic field amplitudes associated with momentum-correlated atomic pairs, which enhances the production of molecules with momentum $2k_L$. If the sum frequency coupling strength is significantly weaker than the second harmonic coupling strength, $\gamma_2 \ll \gamma$, the wave mixing process induces correlations between atoms in the same momentum state, and these momentum correlations align more closely with the Bell state $|\Phi^-\rangle$. In our experiment, we demonstrate the matter-wave analogue of optical up-conversion using a Feshbach resonance, whereas molecular dissociation in the quantum-degenerate regime is analogous to parametric down-conversion, which likewise generates non-classical correlations.

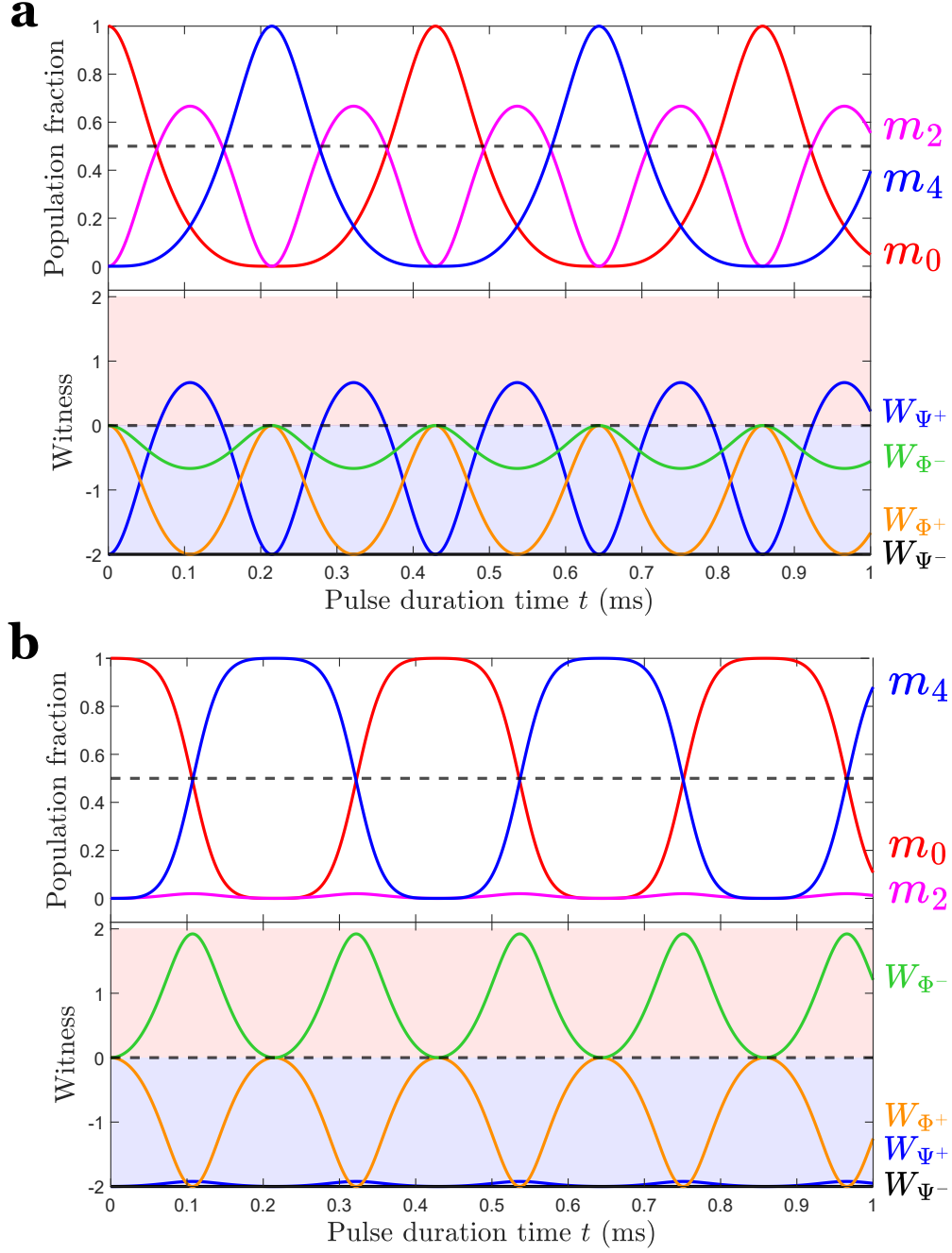


Figure 4.5: **Coupling-dependent sensitivity of entanglement witnesses.** Time evolution of molecular populations (top) and corresponding witness expectation values (bottom) at different coupling strengths. **a**, Coupling strength ratio of $\gamma_2/\gamma = 1$. A non-negative value of $W_{\Psi^+} = 2/3$ indicates that the momentum correlations generated during the reaction align with the Bell state $|\Psi^+\rangle = (|0, 2k_L\rangle + |2k_L, 0\rangle)/\sqrt{2}$. **b**, Coupling strength ratio of $\gamma_2/\gamma = 0.1$. A witness value of $W_{\Phi^-} \approx 2$ indicates that the momentum correlations generated during the reaction overlap almost completely with the Bell state $|\Phi^-\rangle = (|0, 0\rangle - |2k_L, 2k_L\rangle)/\sqrt{2}$, reflecting the propensity for same-state correlations due to the weaker coupling.

CHAPTER 5

OUTLOOK

5.1 Reaction interferometry

Coherent control of chemical reactions has long been a central goal in chemistry. In optochemistry, the reaction outcome can be steered by controlling electronic and nuclear motion in molecules via precise manipulation of the optical waveform of ultrashort laser fields [42]. On the other hand, in the quantum degenerate regime – where reactants can be prepared in coherent superpositions of quantum states, such as nuclear and electronic spin states – each reactant carries a well-defined quantum mechanical phase. These phases can be tuned so that specific reaction pathways interfere constructively or destructively, thereby controlling the outcome of the reaction [43, 44].

Here we demonstrate this with a simplified example. We first prepare an atomic wavefunction in a coherent superposition of three momentum modes, 0 and $\pm 2k_L$, using Kapitza-Dirac diffraction. In the plane-wave representation, this wavefunction takes the form

$$\psi_a(x) = c_{-2}e^{-2ik_Lx} + c_0 + c_2e^{2ik_Lx}. \quad (5.1)$$

The probability amplitudes are obtained by solving the coupled differential equations provided in Eq. (2.13),

$$\begin{aligned} i\hbar\dot{c}_{-2} &= \left(4E_R + \frac{V_0}{2}\right)c_{-2} + \frac{V_0}{4}c_0, \\ i\hbar\dot{c}_2 &= \left(4E_R + \frac{V_0}{2}\right)c_2 + \frac{V_0}{4}c_0, \\ i\hbar\dot{c}_0 &= \frac{V_0}{2}c_0 + \frac{V_0}{4}(c_{-2} + c_2). \end{aligned} \quad (5.2)$$

Solving these coupled equations yields

$$c_0 = \left\{ \cos \left(\frac{\sqrt{V_0^2 + 32E_R^2}t}{2\sqrt{2}\hbar} \right) + \frac{i4\sqrt{2}E_R}{\sqrt{V_0^2 + 32E_R^2}} \sin \left(\frac{\sqrt{V_0^2 + 32E_R^2}t}{2\sqrt{2}\hbar} \right) \right\} e^{-\frac{i(V_0+4E_R)t}{2\hbar}}$$

$$c_{-2} = c_2 = -\frac{iV_0}{\sqrt{2V_0^2 + 64E_R^2}} \sin \left(\frac{\sqrt{V_0^2 + 32E_R^2}t}{2\sqrt{2}\hbar} \right) e^{-\frac{i(V_0+4E_R)t}{2\hbar}}.$$

Here we allow the probability amplitudes to evolve for $t = \sqrt{2}\pi\hbar/\sqrt{V_0^2 + 32E_R^2}$. After turning off the lattice coupling, we allow $\psi_a(x)$ to acquire a time-dependent phase during free evolution. Eq. (5.1) then becomes

$$\psi_a(x, t') = c_{-2}e^{-i4E_R t'/\hbar}e^{-2ik_L x} + c_0 + c_2e^{-i4E_R t'/\hbar}e^{2ik_L x}. \quad (5.3)$$

After a period of free evolution, we pair the atoms into molecules. The molecular wavefunction, given by $\psi_m = \psi_a^2$, can then be explicitly written out as

$$\begin{aligned} \psi_m = & 2c_{-2}c_0e^{-i4E_R t'/\hbar}e^{-2ik_L x} + 2c_0c_2e^{-i4E_R t'/\hbar}e^{2ik_L x} + 2c_{-2}c_2e^{-i8E_R t'/\hbar} \\ & + c_{-2}^2e^{-i8E_R t'/\hbar}e^{-4ik_L x} + c_2^2e^{-i8E_R t'/\hbar}e^{4ik_L x} + c_0^2 \end{aligned} \quad (5.4)$$

Thus, the molecular momentum state populations are given by

$$\begin{aligned}
|\langle -4k_L | \psi_m \rangle|^2 &= |c_{-2}^2|^2 = \frac{V_0^4}{4(V_0^2 + 32E_R^2)^2}, \\
|\langle 4k_L | \psi_m \rangle|^2 &= |c_2^2|^2 = \frac{V_0^4}{4(V_0^2 + 32E_R^2)^2}, \\
|\langle -2k_L | \psi_m \rangle|^2 &= 4|c_{-2}c_0|^2 = \frac{64E_R^2 V_0^2}{(V_0^2 + 32E_R^2)^2}, \\
|\langle 2k_L | \psi_m \rangle|^2 &= 4|c_0c_2|^2 = \frac{64E_R^2 V_0^2}{(V_0^2 + 32E_R^2)^2}, \\
|\langle 0 | \psi_m \rangle|^2 &= |c_0^2 + 2c_{-2}c_2 e^{-i8E_R t/\hbar}|^2 \\
&= \frac{V_0^4 + 1024E_R^4 + 64E_R^2 V_0^2 \cos(8E_R t/\hbar)}{(V_0^2 + 32E_R^2)^2}.
\end{aligned} \tag{5.5}$$

All molecular state populations remain constant, with the exception of $|\langle 0 | \psi_m \rangle|^2$ which oscillates with frequency $8E_R/\hbar = 2\pi \times 10.608$ kHz. Molecules with momentum $k = 0$ can either be created by pairing two atoms with $k = 0$ or by pairing one atom at $k = -2k_L$ with another at $k = 2k_L$. The reaction outcome is influenced by the phase accumulated by atoms with $\pm 2k_L$, $\phi_2(t') = 4E_R t'/\hbar$, which leads to constructive or destructive interference. These results show that quantum interference between different reaction pathways can enhance or suppress the production of molecules. This process is analogous to a Mach–Zehnder interferometer, which uses two beamsplitters to split and recombine a wave, with the final output determined by the relative phase accumulated along the two paths. In the matter-wave picture, coherent atom–molecule coupling plays the role of the beamsplitters, and the relative phase accumulated by the atomic modes determines the final reaction outcome, hence the name reaction interferometer.

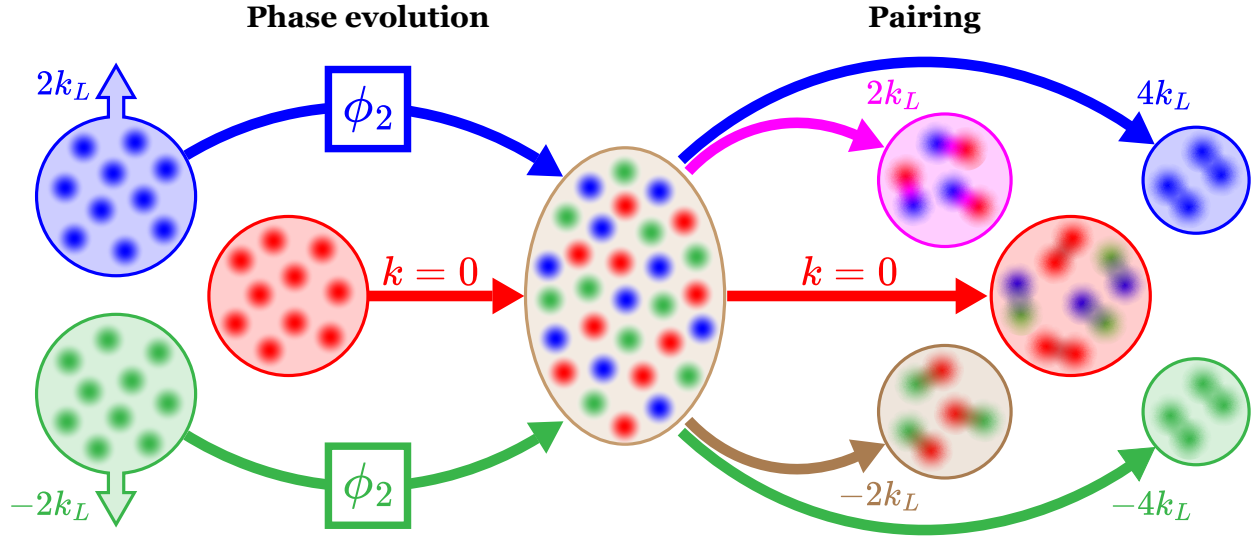


Figure 5.1: **Reaction interferometer.** Atoms are prepared in a coherent superposition of three momentum states, $k = 0$ and $\pm 2k_L$. Momentum states $\pm 2k_L$ accumulate an additional phase ϕ_2 in the trap after lattice coupling is turned off. After free evolution, atoms are paired into molecules with different momenta. With the exception of $k = 0$, molecule creation proceeds through a single reaction pathway. In contrast, molecules with $k = 0$ can be created in two distinct ways: by pairing two atoms with $k = 0$ or by pairing atoms with opposite momenta $\pm 2k_L$. Quantum interference between multiple reaction pathways can enhance or suppress reaction outcomes, depending on the phase $\phi_2(t)$ accumulated during free evolution.

APPENDIX A

DERIVATION OF DIMENSIONLESS MATHIEU EQUATION FOR ATOMS AND MOLECULES

The Hamiltonian of a single particle in a 1D lattice is given by

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_0 \cos^2(kx) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{V_0}{2}(1 + 2 \cos 2kx). \quad (\text{A.1})$$

Therefore the Schrodinger equation is

$$H\psi = E\psi \rightarrow \frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \left(E - \frac{V_0}{2} - \frac{V_0}{2} \cos 2kx \right) \psi = 0. \quad (\text{A.2})$$

Substituting $u = kx$ and $\frac{d^2}{dx^2} = k^2 \frac{d^2}{du^2}$ into Eq. (A.2) yields

$$\frac{\hbar^2 k^2}{2m} \frac{d^2\psi}{du^2} + \left(E - \frac{V_0}{2} - \frac{V_0}{2} \cos 2u \right) \psi = 0. \quad (\text{A.3})$$

Dividing both sides of (A.3) by $\frac{\hbar^2 k^2}{2m} = E_R$ yields

$$\frac{d^2\psi}{du^2} + \left(\left(\frac{E}{E_R} - \frac{1}{2} \frac{V_0}{E_R} \right) - \frac{1}{2} \frac{V_0}{E_R} \cos 2u \right) \psi = 0. \quad (\text{A.4})$$

Replacing $\epsilon = \frac{E}{E_R} - \frac{1}{2} \frac{V_0}{E_R}$ and $\nu = \frac{1}{4} \frac{V_0}{E_R}$, we obtain the Mathieu equation

$$\frac{d^2\psi}{du^2} + (\epsilon - 2\nu \cos 2u)\psi = 0, \quad (\text{A.5})$$

for which the solution $\psi(u)$ takes the Bloch form, $\psi(u) = e^{i(q/k)u} f(u)$, where q is the quasimomentum and $f(u)$ is a π -periodic function because $\cos 2u = \cos(2(u + \pi))$. The Mathieu equation yields even solutions when $\epsilon = \epsilon_a(q/k, \nu)$ and odd solutions when $\epsilon = \epsilon_b(q/k, \nu)$ where $\epsilon_a(q/k, \nu)$ and $\epsilon_b(q/k, \nu)$ are the even and odd Mathieu characteristic values.

Therefore the dimensionless eigenenergies are given by

$$\frac{E}{E_R} = \epsilon_a(q/k, \nu) + \frac{1}{2} \frac{V_0}{E_R} \quad (\text{even parity}), \quad (\text{A.6})$$

$$\frac{E}{E_R} = \epsilon_b(q/k, \nu) + \frac{1}{2} \frac{V_0}{E_R} \quad (\text{odd parity}). \quad (\text{A.7})$$

To derive the Mathieu equation for molecules, we first multiply the mass by two in Eq. (A.3) which yields

$$\frac{\hbar^2 k^2}{4m} \frac{d^2 \psi}{du^2} + \left(E - \frac{V_0}{2} - \frac{V_0}{2} \cos 2u \right) \psi = 0. \quad (\text{A.8})$$

Dividing both sides of (A.8) by $\frac{\hbar^2 k^2}{2m} = E_R$ and rearranging the equation gives us

$$\frac{d^2 \psi}{du^2} + \left(2 \left(\frac{E}{E_R} - \frac{1}{2} \frac{V_0}{E_R} \right) - \frac{V_0}{E_R} \cos 2u \right) \psi = 0. \quad (\text{A.9})$$

Replacing $\epsilon' = 2 \frac{E}{E_R} - \frac{V_0}{E_R}$ and $\nu' = \frac{1}{2} \frac{V_0}{E_R}$, we recover the Mathieu equation

$$\frac{d^2 \psi}{du^2} + (\epsilon' - 2\nu' \cos 2u) \psi = 0. \quad (\text{A.10})$$

Thus the dimensionless molecular eigenenergies are given by

$$\frac{E}{E_R} = \frac{1}{2} \left(\epsilon'_a(q/k, \nu') + \frac{V_0}{E_R} \right) \quad (\text{even parity}), \quad (\text{A.11})$$

$$\frac{E}{E_R} = \frac{1}{2} \left(\epsilon'_b(q/k, \nu') + \frac{V_0}{E_R} \right) \quad (\text{odd parity}). \quad (\text{A.12})$$

APPENDIX B

MOLECULAR VORTICES

Our first attempt to demonstrate phase doubling began with experiments on quantum vortices. Molecular pairing is expected to double the phase of a vortex in an atomic BEC. To deterministically create vortices, we use the chopsticks method pioneered by Anderson [45, 46]. We first create a hole in the BEC using a 780 nm laser. This hole splits into two different holes with one hole moving towards the center of the BEC while the other one moves outwards towards the edge. The moving beams twist the condensate phase, and the resulting quantized circulation produces vortices. The circulation around any closed loop in a superfluid must satisfy

$$\oint v \cdot dl = \frac{\hbar}{m}l, \quad (\text{B.1})$$

where v is the superfluid velocity field and l is an integer that specifies the vortex charge. The two beams generate a vortex–antivortex pair, which circulate in opposite directions. In our experiment, we require only a single vortex, so we remove the antivortex by dragging it out of the condensate. The moving beams are generated by a digital micromirror device (DMD), which plays a sequence of frames to produce the desired motion. The beams move at 20% of the speed of sound to avoid nucleating additional vortices. The probability of creating singly quantized vortices using the chopsticks method exceeds 80%.

To detect the vortices, we perform time-of-flight (TOF) imaging. The healing length, which sets the characteristic size of a vortex core, is defined as

$$\xi = \frac{\hbar}{\sqrt{2mg_{3\text{D}}n_c}}, \quad (\text{B.2})$$

where $g_{3\text{D}} = 4\pi\hbar^2 a/m$ is the 3D interaction strength with a the atomic scattering length. The healing length is inversely proportional to the condensate density n_c . We can estimate the vortex core size in two dimensions with the 2D interaction strength $g_{2\text{D}} = g_{3\text{D}}/\sqrt{2\pi}l_z$,

where $l_z = \sqrt{\hbar/m\omega_z}$ is the harmonic oscillator length and ω_z is the longitudinal trap frequency of the vertical lattice. Using g_{2D} , Eq. (B.2) yields a healing length of $\xi \approx 0.3 \mu\text{m}$ at $\omega_z = 2\pi \times 400 \text{ Hz}$, $a = 180a_0$ and $n_{2D} = 50 \mu\text{m}^{-2}$, which is more than three times smaller than our imaging resolution of $\approx 1.1 \mu\text{m}$. To increase the vortex core size, we perform TOF. During TOF expansion, the healing length ξ increases as the condensate density n_c decreases. We first turn off the DMD potential and then shut off the vertical lattice for 3D TOF, since the BEC is much more tightly confined by the vertical lattice. The levitation gradient is turned on during TOF to prevent the BEC from falling out of focus. We confirm the existence of a vortex using TOF for 20 ms in Fig. B.1.

To create molecular vortices, we create vortices in the atomic BEC first and then shut off the beam pinning the vortex to the center of the BEC. After waiting for 10 ms, we convert the atomic BEC into a molecular BEC and blow away any remaining atoms after turning off Feshbach coupling. To detect the molecular vortex, we perform TOF again and confirm the existence of the molecular vortex in Fig. B.2b. To confirm that this density depletion is indeed a molecular vortex, we create a hole in the atomic BEC without dragging any beams across the sample and shut off the beam before pairing the atoms into molecules. When we perform TOF on this molecular sample, we do not detect any density depletion, see Fig. B.2a, confirming that the density depletion detected inside the molecular BEC was indeed a molecular vortex.

To measure the phase winding of both atomic and molecular vortices, we perform BEC interferometry in free space during TOF. We demonstrate this method first on vortices in the atomic BEC. The atomic BEC is split into two sections: an inner circle and an outer ring. A vortex is created only inside the inner circle. Thus, the atomic wavefunction can be described as $\psi_a = e^{i\varphi_a} + 1$ since the outer ring carries no phase, which gives us $n_a = |\psi_a|^2 = 2 + 2\cos\varphi_a$. Interference fringes arise from the second term, whose oscillatory phase factor produces spatial modulation. By quenching the atomic scattering length to zero

and letting the inner circle and outer ring interfere in free space, we obtain interference fringes with a single spiral pattern, see Fig. B.3. On the other hand, when we prepare a doubly quantized vortex in the inner circle, the atomic wavefunction is given by $\psi_a = e^{i2\varphi_a} + 1$, which gives us $n_a = |\psi_a|^2 = 2 + 2\cos 2\varphi_a$. By letting the inner circle and outer ring interfere, we obtain interference fringes with a double spiral pattern, see Fig. B.3. The doubly quantized vortex in the atomic BEC is created by combining two vortices of the same circulation using the chopsticks. Because the molecular phase winds twice as fast as the atomic phase, molecular vortices should produce interference fringes with a double spiral pattern. However, we were unable to observe distinct interference fringes with the molecular BEC. This led us to consider other methods to show phase doubling, eventually settling on phase imprinting with optical lattices.

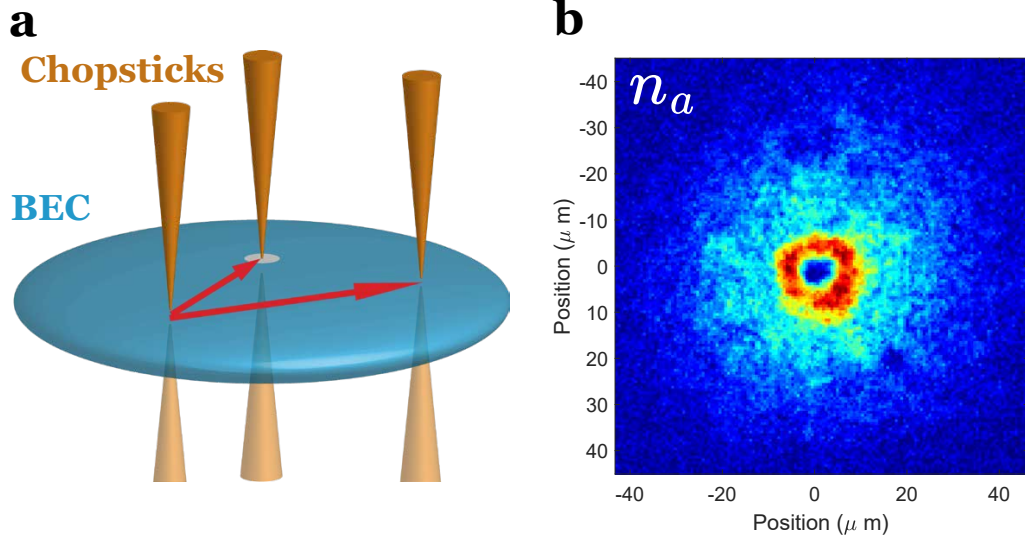


Figure B.1: **Vortex creation.** **a**, Deterministic generation of singly quantized vortices using chopsticks method. Two beams are dragged across the BEC. One beam pins a vortex to the center of the BEC while the other beam drags the other vortex out of the BEC. **b**, Detection of vortices using time-of-flight (TOF). The DMD potential is shut off first and then the vertical lattice potential. TOF increases the healing length which enlarges the vortex core.

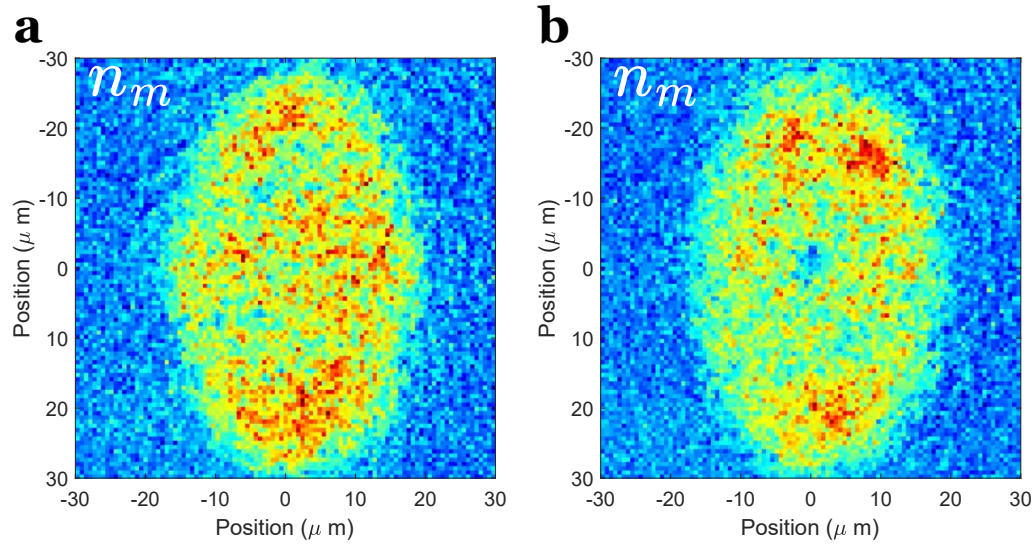


Figure B.2: **Molecular vortex.** **a**, A hole is created in an elliptical atomic BEC using a beam. The beam is shut off before paring the atoms into molecules and blowing away remaining atoms. TOF reveals no vortex. **b**, A vortex is created in an elliptical atomic BEC using the chopsticks method. The beam pinning the vortex to the center of the BEC is shut off before paring the atoms into molecules and blowing away remaining atoms. TOF reveals a molecular vortex.

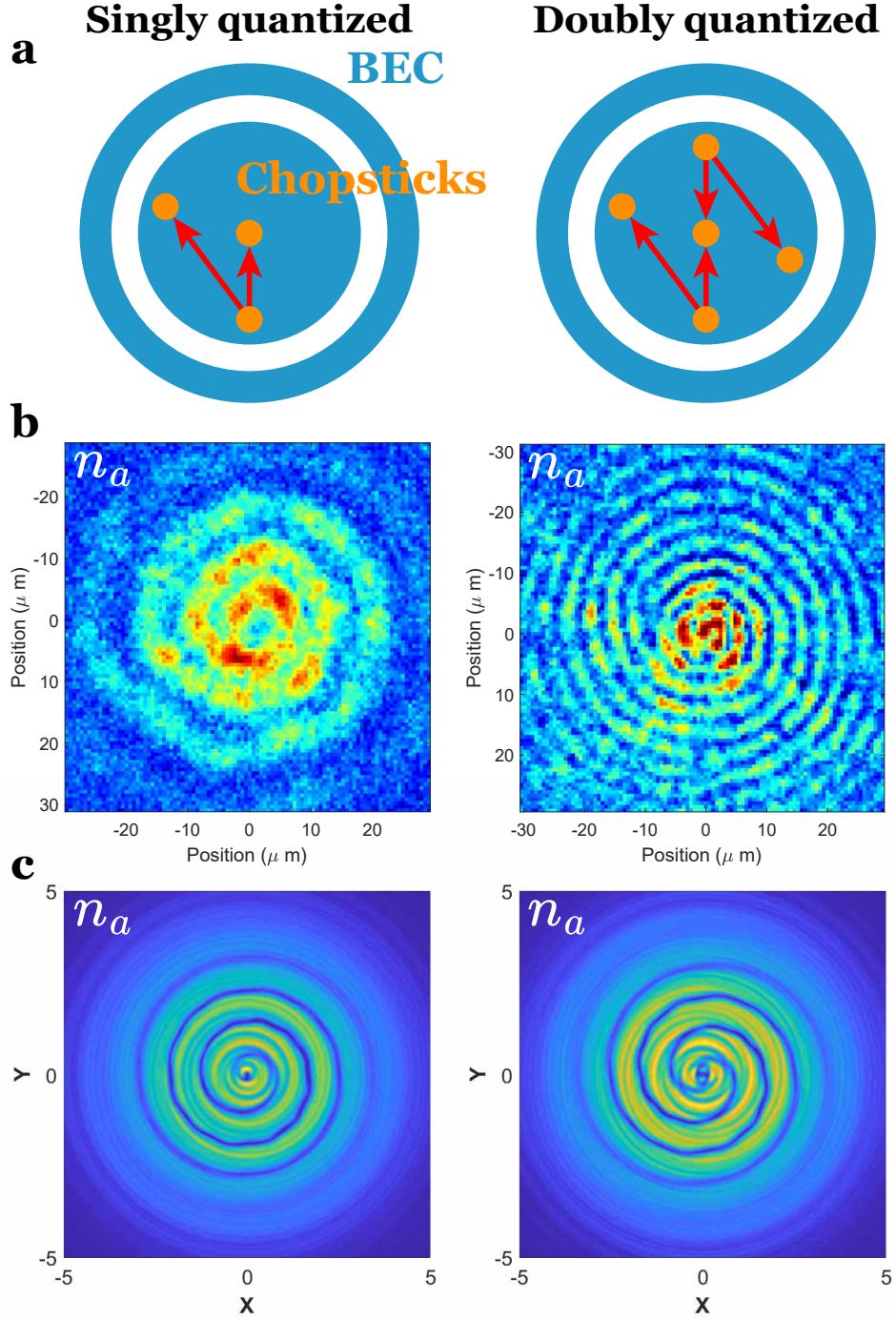


Figure B.3: **Vortex interferometry.** **a**, Chopsticks scheme for creating singly and doubly quantized vortices. Atomic BEC is split into two sections: an inner circle and outer ring. Vortices are created only in inner circle. **b**, Vortex spiral interference fringes after TOF. The atomic interaction strength is quenched to zero right before TOF. A single spiral emerges for a singly quantized vortex, whereas a double spiral emerges for a doubly quantized vortex. **c**, Gross-Pitaevskii simulation of vortex interference.

APPENDIX C

LIST OF PUBLICATIONS

1. **Shu Nagata**, Tadej Meznarsic, Chuixin Kong and Cheng Chin. Phase Doubling and Entanglement in Coherent Many-Body Chemical Reactions. arXiv:2505.20581.
2. Ke Wang, Zhendong Zhang, **Shu Nagata**, Zhiqiang Wang and Kathryn Levin. Universal coherent atom-molecule oscillations in the dynamics of the unitary Bose gas near a narrow Feshbach resonance. Phys. Rev. Research **7**, L012025 (2025).
3. Youjia Huang, **Shu Nagata**, Joseph Jachinowski, Jiazhong Hu and Cheng Chin. Two-dimensional arrays of Bose-Einstein condensates: Interference and stochastic collapse dynamics. Phys. Rev. Research **6**, 043272 (2025).
4. Zhiqiang Wang, Ke Wang, Zhendong Zhang, **Shu Nagata**, Cheng Chin and Kathryn Levin. Stability and dynamics of atom-molecule superfluids near a narrow Feshbach resonance. Phys. Rev. A **110**, 013306 (2024).
5. Zhendong Zhang, **Shu Nagata**, Kai-Xuan Yao and Cheng Chin. Many-body chemical reactions in a quantum degenerate gas. Nature Physics **19**, 1466–1470 (2023).

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