Spin Liquid Condensate of Spinful Bosons

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We introduce the concept of a bosonic spin liquid condensate (SLC), where spinful bosons in a lattice form a Bose-Einstein condensate (BEC) which is a total spin singlet and does not break the spin rotation symmetry. It has an energy gap to all spin excitations. The realization of this SLC requires the spin of the bosons to be $S \geq 2$. We give the phase diagram for the spin 2 case using a variational wave function method, and verify the existence of an SLC phase. We show there is a direct analogy between SLC and the resonating-valence-bond (RVB) state.

Bose-Einstein condensate (BEC) is known as a bosonic many-body state characterized by a spontaneously broken global U(1) symmetry. With the development of cold atom techniques in the past decades [1], the BEC of spinful bosons has attracted a great deal of attention. Compared to scalar bosons which only have a U(1) symmetry, spinful bosons possess an additional SU(2) spin rotational symmetry. It is generally believed that spinful bosons at low temperatures condense into a spinor BEC, which has a spinor order parameter that breaks both the U(1) and the SU(2) symmetries [2–10]. A natural question to ask is then whether a spin rotationally invariant BEC at zero temperature. It possesses a spin liquid condensate (SLC), which is a robust spin rotation symmetry. It has an energy gap to all spin excitations. The realization of this SLC requires the spin of the bosons to be $S \geq 2$. We give the phase diagram for the spin 2 case using a variational wave function method, and verify the existence of an SLC phase. We show there is a direct analogy between SLC and the resonating-valence-bond (RVB) state.

Bosons in a translationally invariant lattice fall into either a Mott insulator or a BEC superfluid at zero temperature [20]. In a Mott insulator where interaction dominates, all the sites are in the lowest on-site state with a definite particle number $n$. As the hopping between the sites increases, they prefer a coherent superposition of several on-site states with different particle numbers to gain the kinetic energy, and the Mott insulator turns into a BEC. Usually, for spin $S$ bosons, the coherent superposition induces a non-vanishing spinor order parameter $\varphi_m = \langle \psi_{i,m} \rangle$, and one obtains a spinor BEC that breaks both the U(1) and SU(2) symmetries. However, suppose now the lowest two on-site states are spin singlet states close to each other in energy, while all the other states have much higher energies. In this case, the sites may prefer a superposition of the two singlet states only, resulting in a spin singlet BEC with $\langle \psi_{i,m} \rangle = 0$ protected by the spin rotational symmetry. However, it is possible to construct a non-vanishing order parameter which carries one unit of charge with total spin zero (see Eq. (2)). This is the key idea here for the concept of spin liquid condensate (SLC).

To find such a system explicitly, we examine the spin Bose Hubbard model widely used for describing spin $S$ bosons in a lattice. The Hamiltonian $H = H_I + H_t$ can be written in the following two parts:

$$H_I = -\mu \sum_i \hat{n}_i + \frac{1}{2} \sum_{i,j} \left[ \sum_{m=0}^S U_{2J} \mathcal{P}_{ij}^S \right],$$

$$H_t = -\sum_{\langle ij \rangle, m} \left( \hat{\psi}_{i,m}^\dagger \hat{\psi}_{j,m} + h.c. \right),$$

(1)

where $\mu$ is the chemical potential, $U_{2J} \geq 0$ is the on-site Hubbard interaction energy between two bosons of total spin $2J$, and $t$ is the nearest hopping amplitude. $i$ and $j$ label the lattice sites, while $m$ denotes the spin $z$ component. $\hat{n}_i = \sum_m \hat{\psi}_{i,m}^\dagger \hat{\psi}_{i,m}$ is the particle number on site $i$. The non-negative projection operator $\mathcal{P}_{ij}^S$ is defined as $\mathcal{P}_{ij}^S = \sum_m A_{2Jm}(i) A_{2Jm}(j)$ with $A_{2Jm}(i) = \sum_{m'} \langle 2J, m | S, m' ; S, m - m' | \psi_{i,m}^\dagger \psi_{i,m} \rangle$, where $\langle 2J, m | S, m' ; S, m - m' \rangle$ is the Clebsch-Gordan co-
efficient. The on-site state energy spectrum is then obtained by diagonalizing the interaction part $H_I$. For spin $S = 1$ bosons, one can show it is impossible to have the lowest two on-site states to both be spin singlets, and the idea of SLC can not be applied. However, this is in general possible for bosons with spin $S \geq 2$.

As a simple example, we study spin 2 bosons in this letter to see how an SLC can be realized. First, we need to find a regime of parameters where the lowest two on-site states are singlet states. Generally, the on-site states can be labeled as $|n, l, m, \gamma\rangle_i$, where $n$ is the particle number, $l$ is the total spin of the $n$ particles, $m$ is the $z$-component of the total spin, and $\gamma$ represents the other quantum numbers [21]. In our discussion, we shall omit the label $\gamma$, since all the states involved are distinguishable through their $n, l, m$ labels. The minimal two singlet states of spin 2 bosons are the dimer state $|2, 0, 0\rangle_i$ and the trimer state $|3, 0, 0\rangle_i$, formed by two and three bosons respectively [21][22]. We find when $U_0 < U_2 < 36U_4/85$ and $\mu = \mu_0 = 3U_2 - U_0$, the dimer state and the trimer state become degenerate and have the lowest on-site energy. To see this explicitly, we have plotted the on-site state energy spectrum for $U_4 = 3U_2 = 30U_0$ and $\mu = \mu_0 - \Delta$ in Fig. 1. The on-site energy of each state $|n, l, m\rangle_i$ is denoted by $E_{nl}$. An easy calculation shows that $E_{30} - E_{20} = \Delta$. For later convenience, we define $E_a$ as the energy difference between the third and the lowest energy levels, as is shown in Fig. 1. The desired regime is then $|\Delta| \ll E_a$.

Then, for this ground state in this regime to be an SLC, there must also be a large enough transition amplitude between the two on-site states $|2, 0, 0\rangle_i$ and $|3, 0, 0\rangle_i$. As always, the transition amplitude originates from the kinetic hopping term $H_I$. However, the tunneling from $|2, 0, 0\rangle_i$ to $|3, 0, 0\rangle_i$ cannot be accomplished by a single hop, which would necessarily change the on-site state $|2, 0, 0\rangle_i$ to a state with total spin $l = 2$. For the transition to occur, the site must hop with its nearby sites for at least three times. In such a transition, the site has to experience two intermediate states of energy of order $E_a$, as is shown in Fig. 1. According to the perturbation theory, this mechanism gives us a effective hopping amplitude between the singlet dimer state and the trimer state $t_{eff} = t^3/E_a^2$. When the hopping amplitude increases to $|t_{eff}/\Delta| \sim 1$, the system would prefer a coherent superposition of the dimer and trimer states and become a condensate. While at the same time, the condition $|\Delta| \ll E_a$ ensures that $|t/E_a| \ll 1$, so the superposition with any other states is not favorable yet, and the condensate is identified as an SLC. We can write down a rotationally invariant order parameter for this SLC that breaks the U(1) symmetry:

$$\lambda = \langle \sum_{m, m'} D_{m'm} \psi_{i,m'}^\dagger \psi_{i,m} \rangle,$$  \hspace{1cm} (2)

where the coefficient $D_{m'm} = (-1)^{m + m'} \langle 0, 0|2, -m - m'|2, m + m'|2, 2, m \rangle$. This order parameter simply represents the superposition of $|2, 0, 0\rangle_i$ and $|3, 0, 0\rangle_i$ via three-time hoppings. Under a U(1) rotation $e^{i\phi}$ the order parameter transforms as $\lambda \rightarrow e^{i\phi}\lambda$, thus the minimal flux of a superfluid vortex is $2\pi$, which implies the low energy elementary excitation has charge 1. This is a prominent difference between SLC and the spin-paired BEC with elementary charge 2 [11].

To see the existence of the SLC phase explicitly, we propose a variational wave function for the ground state of the system:

$$|SLC\rangle = Sym \prod_{(ij)} \left[u + \sum_m \left(\psi_{i,m}^\dagger \psi_{j,m} + h.c.\right)\right] \times \prod_i \left(\alpha|2, 0, 0\rangle_i + \beta|3, 0, 0\rangle_i\right),$$ \hspace{1cm} (3)

in terms of variational parameters $u$, $v$ and $\alpha$, $\beta$ satisfying $|\alpha|^2 + |\beta|^2 = 1$. The notation $Sym$ represents a symmetrization of all bonds of nearest sites $(ij)$ so that the wave function is independent of the sequence of $(ij)$ in the product. The product operator in the front defined on bonds $(ij)$ comes from the quantum fluctuation
induced by $H_1$, and establishes the correlation between different lattice sites. In the limit $|t/E_a| \ll 1$, a simple estimation gives $v/u \sim |t/E_a|$, and the quantum fluctuation is weak. However, it is indispensable in the calculation of the energy contribution from the three-time hoppings. One can then minimize the variational energy per site $E_G$ up to the quadratic order $|v/u|^2$. Without loss of generality, we choose to set $t$ real and positive, and $\alpha$, $\beta$ real. Up to the quadratic order, the normalization condition for the wave function is given by $|u|^2 + 2z(2 + \beta^2)(7 + \beta^2)|v|^2/5 = 1$, where $z$ is the number of nearest neighbours of a site. After some calculations, the variational energy $E_G$ can be expressed as [23]:

$$E_G = |u|^2 \beta^2 \Delta - \frac{2}{5} z t \text{Re}(u) \text{Re}(v) (2 + \beta^2) (7 + \beta^2)$$

$$- \frac{36}{5} z t |v|^2 (1 - \beta^2)^2 + \frac{1}{5} z^2 |v|^2 V(\beta^2),$$

(4)

where $V(\beta^2)$ is a quadratic function of $\beta^2$ given in the supplementary material [24], which is of order $E_a$. In particular, we minimize the variational energy function $E_G$ for $U_4 = 3U_2 = 30U_0$ and $z = 4$, and the phase diagram is shown in Fig. 2. The SLC phase occurs as we expected. The regime of spinor BEC is obtained separately by a Gutzwiller method used in many studies [23]. In the limit $|t/E_a| \ll 1$, the phase boundaries between SLC and the Mott insulators take the following form:

$$\Delta + a_{\pm} \frac{z t^2}{E_a} = \pm b_{\pm} \frac{z t^2}{E_a},$$

(5)

where $a_{\pm}$ and $b_{\pm}$ are dimensionless factors depending on the interaction parameters $U_{2,4}$ only. This result agrees with our expectation for the phase transition $|t_{eff}/\Delta| \sim 1$, except for that the on-site energy difference $\Delta = \Delta + a_{\pm} z t^2/E_a$ has a second order energy correction due to the virtual hoppings. The SLC finally becomes unstable against quantum fluctuations when $|t/E_a| \sim 1$, and a spinor BEC phase takes charge.

We now take a closer look at the SLC state, and show it has an energy gap to all spin excitations. To possess charge superfluidity, particles in the SLC have to move around and undergo macroscopic ring exchanges [24]. However, the motion of the particles must not break the spin rotational symmetry. This is naturally achieved through the three-time hopping process. As is shown in Fig. 3(a), suppose a particle in a trimer state is to move to a nearby site dimer state on the right. After hopping once, both sites become high energy states with total spin $l = 2$. Due to the spin rotational symmetry of $H_1$, they form a spin singlet valence bond of length 1. To lower the energy, the particle must hop back to the left site and then forward to the right site again, so that the left and right sites become the dimer and trimer states respectively, and the spin singlet valence bond disappear. By such a process, the particles are able to move around in the lattice, while spin singlet valence bonds are created and erased resonantly. In principle, via more times of hoppings, singlet valence bonds of length larger than 1 can arise, as is shown in Fig. 3(b). SLC is in this sense analogous to the dopped RVB state suggested by Anderson for high temperature cuprates [15, 16, 29], where electrons form resonating valence bonds while breaking the U(1) symmetry. According to Eq. (3), the amplitude for creating a singlet valence bond of length $L$ is approximately $(v/u)^L \propto (t/E_a)^L$, decaying exponentially as a function of $L$. The singlet valence bonds in
SLC are thus short range, and all the spin excitations should be gapped. The spin correlation length is therefore \( \xi_S \approx 1/\ln(r_c/E_a/t) \), where \( r_c = (t/E_a) \), is the critical value for the phase transition from SLC to a spinor BEC.

By Goldstone theorem, however, SLC should have a gapless mode that is spinless, corresponding to the broken U(1) symmetry. This mode can be derived at low energies by perturbing the wave function in Eq. (3). For convenience, we rewrite \( \psi_{i,m} = \sqrt{n_i,m} e^{i\phi_{i,m}} \), where \( n_i,m \) and \( \phi_{i,m} \) satisfies \( \hat{n}_i,m, \phi_{i,m} = i\delta_{ij}\delta_{mm'} \). The global phase can then be expressed as \( \phi_i = \sum_m \phi_{i,m}/5 \), which is rotationally invariant and satisfies the commutation relation \( \hat{n}_i, \phi_j = i\delta_{ij} \), where \( \hat{n}_i \) is the particle number. We denote the fluctuations of particle number and global phase by \( \delta\hat{n}_i = \hat{n}_i - \langle \hat{n}_i \rangle \) and \( \delta\phi_i = \phi_i - \langle \phi_i \rangle \). With \( \alpha \) and \( \beta \) real and positive, we have \( \langle \hat{n}_i \rangle = 2 + \beta^2 \) and \( \langle \phi_i \rangle = 0 \). By adding the two fluctuations \( \delta\hat{n}_i \) and \( \delta\phi_i \) to the variational wave function in Eq. (3), one obtains an low energy effective Hamiltonian:

\[
H_{\text{eff}} = \sum_k \left[ \frac{1}{8\beta^2} \frac{d^2\mathcal{E}_G}{d\beta^2} \delta\hat{n}_k \delta\hat{n}_{-k} + \frac{18}{5} z t|v|^2 (1 - \beta^2) \beta^2/k^2 \delta\phi_k \delta\phi_{-k} \right],
\]

where \( d \) is the dimension of the system. This is a Hamiltonian of harmonic oscillators that can be easily diagonalized, and hence we get a linear energy dispersion \( \omega_k = v_s k \), where \( v_s = \sqrt{9zt|v|^2(1 - \beta^2)(d^2\mathcal{E}_G/d\beta^2)/5d} \) is the superfluid velocity. In the limit \( t/E_a \ll 1 \), the velocity is asymptotically \( v_s \propto \alpha\beta t^{5/2}/E_a^{3/2} \). This linear Goldstone mode is obviously spinless, and thus describes the charge fluctuations only. The distinct energy dispersions of spin and charge excitations naturally lead to a spin-charge separation in SLC.

Being a spin rotationally invariant condensate, SLC is necessarily a fragmented BEC \cite{13}. In the long range limit, the one-particle density matrix of SLC has the form

\[
\rho_{mm'}^{(1)}(\mathbf{r}, \mathbf{r}') = \langle \psi_{i,m} \psi_{j,m'}^\dagger \rangle = \delta_{mm'} e^{-|\mathbf{r}_i - \mathbf{r}_j|/\xi_S},
\]

where \( \xi_S \) is the spin correlation length defined in the above. There is thus no eigenvalue of order \( N \) in the one-particle density matrix \( \rho^{(1)} \), meaning that SLC is an extremely fragmented condensate. More importantly, different from most fragmented BECs proposed in the literature which relies on a finite system size, SLC is always robust in the thermodynamic limit.

Though we have only analyzed SLC for spin 2 bosons, the idea of SLC is quite general. For bosons with spin \( S > 2 \) in a lattice, there are more Hubbard parameters \( U_{2,j} \), and more singlet on-site states can be constructed \cite{22}. It is always possible to find a regime where two singlet states have the lowest energies and are nearly degenerate. We therefore expect various SLC phases to exist in these systems.

Finally, we briefly discuss on the experimental realization and observation of SLC in cold atom experiments. The Bose-Hubbard model can be implemented by trapping bosonic atoms into an optical lattice. The Mott-superfluid phase of spinless bosons has been observed in several experiments \cite{19,20,21}. For hyperfine spin 2 atoms \(^{23}\text{Na}, ^{83}\text{Rb} \) or \(^{87}\text{Rb} \) which have been experimentally studied, it is possible to realize an SLC in a lattice if the Hubbard interaction parameters \( U_{2,j} \) can be tuned properly through resonances. Such an SLC can be distinguished from a spinor BEC or a Mott insulator experimentally. The superfluidity of SLC can be verified by single-atom-resolved imaging \cite{30,31}, or by seeing the only Goldstone mode in the Bragg spectroscopy measurement \cite{22}. The spin rotational symmetry can be easily seen through a Stern-Gerlach imaging, since it ensures the populations on all spin components \( m \) to be equal, namely, \( \langle \hat{n}_{i,m} \rangle = \langle \hat{n}_i \rangle/5 \) \cite{22}.

In summary, we have introduced the concept of SLC as a robust spin singlet BEC at zero temperature, and showed it is realizable for spin \( S \geq 2 \) bosons in a lattice. As an example, we construct the SLC phase for spin 2 bosons explicitly, and verify that it has gapped spin excitations and a gapless spinless Goldstone mode, which leads to spin-charge separation. Particles in an SLC move around in accompany with the creation and annihilation of spin singlet valence bonds, which is in analogy to electrons in the RVB state proposed for high temperature cuprates. We further show that SLC is an extremely fragmented BEC that exists in the thermodynamic limit. Lastly, we shortly discussed the possibilities of SLC in the experiments.

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be involved in the later derivations as: 

where $|\Omega\rangle$ is the zero-particle vacuum state of the system. We can also write down the on-site states (normalized) to $i=1$ respectively: 

$$
|2, 0, 0\rangle_i = D^\dagger_i |\Omega\rangle, \quad |3, 0, 0\rangle_i = T^\dagger_i |\Omega\rangle,
$$

(9)

where $|\Omega\rangle$ is the zero-particle vacuum state of the system. We can also write down the on-site states (normalized) to be involved in the later derivations as:

$$
|1, 2, m\rangle_i = \psi^\dagger_{i, m} |\Omega\rangle, \quad |2, 2, m\rangle_i = (-1)^m \frac{\sqrt{5}}{3} \psi^\dagger_{i, -m} T^\dagger_i |\Omega\rangle, \\
|3, 2, m\rangle_i = \frac{\sqrt{5}}{8} \psi^\dagger_{i, m} D^\dagger_i |\Omega\rangle, \quad |4, 2, m\rangle_i = \frac{\sqrt{5}}{8} \psi^\dagger_{i, m} T^\dagger_i |\Omega\rangle.
$$

(10)

As is shown in Fig. 1, these states are the intermediate states experienced by a site during the three-time hopping processes.

With the above explicit expressions, the energies of these on-site states can be obtained straightforwardly. For later convenience, we shall set $E_{20} = 0$ by shifting the interaction Hamiltonian $H_I$ to $H_I = H_I - \sum_i (U_0 - 2\mu)$, which doesn’t change the physics. Assuming the chemical potential is $\mu = \mu_0 - \Delta$ where $\mu_0 = 3U_2 - U_0$, we find the energy levels as follows:

$$
E_{20} = 0, \quad E_{30} = \Delta, \quad E_{12} = 3U_2 - 2U_0 - \Delta, \quad E_{22} = U_2 - U_0, \\
E_{32} = \frac{7}{5} U_0 - \frac{17}{7} U_2 + \frac{36}{35} U_4 + \Delta, \quad E_{42} = \frac{23}{20} U_0 - \frac{3}{2} U_2 + \frac{27}{20} U_4 + 2\Delta.
$$

(11)

### SUPPLEMENTARY MATERIAL

**Derivation and minimization of the variational energy $E_G$**

To derive the variational energy function per site $E_G$, we need to examine the Bose-Hubbard Hamiltonian in more details. We first focus on the on-site interaction $H_I$ to study the on-site energies of them. Following Ref. [21], we define two spin singlet operators $D^\dagger_i$ and $T^\dagger_i$ as below:

$$
D^\dagger_i = \frac{1}{\sqrt{10}} \left( 2\psi^\dagger_{i, +2} \psi^\dagger_{i, -2} - 2\psi^\dagger_{i, +1} \psi^\dagger_{i, -1} + \psi^\dagger_{i, 0}^2 \right),
$$

$$
T^\dagger_i = \frac{1}{\sqrt{420}} \left( 12\psi^\dagger_{i, +2} \psi^\dagger_{i, 0} \psi^\dagger_{i, -2} + 6\psi^\dagger_{i, +1} \psi^\dagger_{i, 0} \psi^\dagger_{i, -1} - 3\sqrt{6}\psi^\dagger_{i, +2} \psi^\dagger_{i, -1}^2 - 3\sqrt{6}\psi^\dagger_{i, -2} \psi^\dagger_{i, +1}^2 - 2\psi^\dagger_{i, 0}^3 \right).
$$

(8)

It can be verified that both $D^\dagger_i$ and $T^\dagger_i$ are rotationally invariant. They create the normalized dimer state and the normalized trimer state appearing in the variational wave function $|\text{SLC}\rangle$ respectively:

$$
|2, 0, 0\rangle_i = D^\dagger_i |\Omega\rangle, \quad |3, 0, 0\rangle_i = T^\dagger_i |\Omega\rangle.
$$

(9)

where $|\Omega\rangle$ is the zero-particle vacuum state of the system. We can also write down the on-site states (normalized) to be involved in the later derivations as:

$$
|1, 2, m\rangle_i = \psi^\dagger_{i, m} |\Omega\rangle, \quad |2, 2, m\rangle_i = (-1)^m \sqrt{\frac{5}{3}} \psi^\dagger_{i, -m} T^\dagger_i |\Omega\rangle, \\
|3, 2, m\rangle_i = \sqrt{\frac{5}{8}} \psi^\dagger_{i, m} D^\dagger_i |\Omega\rangle, \quad |4, 2, m\rangle_i = \sqrt{\frac{5}{8}} \psi^\dagger_{i, m} T^\dagger_i |\Omega\rangle.
$$

(10)

As is shown in Fig. 1, these states are the intermediate states experienced by a site during the three-time hopping processes.

With the above explicit expressions, the energies of these on-site states can be obtained straightforwardly. For later convenience, we shall set $E_{20} = 0$ by shifting the interaction Hamiltonian $H_I$ to $H_I = H_I - \sum_i (U_0 - 2\mu)$, which doesn’t change the physics. Assuming the chemical potential is $\mu = \mu_0 - \Delta$ where $\mu_0 = 3U_2 - U_0$, we find the energy levels as follows:

$$
E_{20} = 0, \quad E_{30} = \Delta, \quad E_{12} = 3U_2 - 2U_0 - \Delta, \quad E_{22} = U_2 - U_0, \\
E_{32} = \frac{7}{5} U_0 - \frac{17}{7} U_2 + \frac{36}{35} U_4 + \Delta, \quad E_{42} = \frac{23}{20} U_0 - \frac{3}{2} U_2 + \frac{27}{20} U_4 + 2\Delta.
$$

(11)
These energies are plotted in Fig. 1 for $U_4 = 3U_2 = 30U_0$, and one can easily see that provided $\Delta$ is small, $E_{20}$ and $E_{30}$ are the lowest two energy levels. In this example, the activation energy $E_a$ is seen to be around $10U_0$.

Before calculating the variational energy $E_G$, we derive the normalization condition for the variational wave function \( \langle SLC \rangle \), which serve as the constraint for the minimization of $E_G$ later. Up to the quadratic order $|v/u|^2$, each site has an amplitude $u$ to hop with its $z$ neighboring sites, so the condition can be approximately written as

\[
1 = \langle SLC | SLC \rangle^{2/N} \approx |u|^2 (\alpha^2 + \beta^2)^2 + 2z|v|^2 \sum_m \left( \alpha^2 \langle 2, 0, 0 | \psi_{i, m}^\dagger \psi_{i, m} | 2, 0, 0 \rangle + \beta^2 \langle 3, 0, 0 | \psi_{i, m}^\dagger \psi_{i, m} | 3, 0, 0 \rangle \right)
\times \left( \alpha^2 \langle 2, 0, 0 | \psi_{j, m} \psi_{j, m} | 2, 0, 0 \rangle + \beta^2 \langle 3, 0, 0 | \psi_{j, m} \psi_{j, m} | 3, 0, 0 \rangle \right)
= |u|^2 + \frac{2}{5}z|v|^2 (2 + \beta^2)(7 + \beta^2),
\]

where $\alpha$ and $\beta$ have been chosen real and positive as is in the paper, and $\alpha^2 + \beta^2 = 1$ is assumed beforehand. Using this constraint, we can substitute $u$ (up to a phase factor) in terms of $v$ and $\beta$ in the future calculations.

Now we derive the expression for the variational energy $E_G = \langle \tilde{H}_f + H_t \rangle / N$ approximated up to the quadratic order $(v/u)^2$. This approximation allows us to discard those spin singlet valence bonds with length longer than $L > 1$, whose probability of arising is of order $(v/u)^2L$. Following this idea, the interaction energy per site is found to be:

\[
\langle \tilde{H}_f \rangle / N \approx |u|^2 \beta^2 \Delta + \frac{1}{5} z|v|^2 V(\beta^2),
\]

where $V(\beta^2)$ is a quadratic function given by

\[
V(\beta^2) = (2 + \beta^2) \left( 7E_{32}(1 - \beta^2) + 8E_{42}\beta^2 \right) + (7 + \beta^2) \left[ 2E_{12}(1 - \beta^2) + 3E_{22}\beta^2 \right].
\]

This can be understood in the following way: a site has amplitude $u$ to be a on-site singlet and amplitude $v$ to form a valence bond with one of its $z$ neighbors, while the energy of a valence bond of length 1 can be shown to be $2V(\beta^2)/5$. The energy expectation of a site is then $|u|^2$ times the on-site singlet energy $\beta^2 \Delta$ plus $(z/2)|v|^2$ times the energy of a valence bond.

Derivation of the hopping energy $\langle H_t \rangle / N$ involves the transition between two total spin $l = 2$ on-site states. By Wigner-Eckart theorem, the transition amplitude has the following form:

\[
\langle n + 1, 2, m_1 | \psi_{i, m_2}^\dagger | n, 2, m_3 \rangle = g(n + 1, n) \langle 2m_1 | 2m_2, 2m_3 \rangle,
\]

where $g(n+1,n)$ is a coefficient depend on $n$ only. A quick calculation yields the coefficients needed here: $g(2, 1) = \sqrt{2}$, $g(3, 2) = 2/\sqrt{7}$, and $g(4, 3) = \sqrt{3}/4$. The hopping energy can then be derived as (with $t$ assumed real and positive):

\[
\langle H_t \rangle / N = -\frac{z}{2} \cdot 2t|v|^2 \alpha^2 \beta^2 \sum_{m_1, m_2} 5 \left( \frac{2}{m_1} \frac{2}{m_2} \frac{2}{m_1 - m_2} \right) \left[ \frac{7}{5} \cdot \frac{4}{7} \cdot \frac{3}{5} + 2 \sqrt{\frac{2}{5} \cdot \frac{7}{5} \cdot \frac{8}{5} \cdot \frac{3}{14} \cdot \frac{3}{5} \cdot \frac{2}{5}} \right]
\times
- \sum_m \frac{z}{2} t(u + u^*)(v + v^*) \frac{2\alpha^2 + 3\beta^2}{5} \cdot \frac{7\alpha^2 + 8\beta^2}{5}
= -\frac{36}{5} z|v|^2 (1 - \beta^2)^2 - \frac{2}{5} z t \text{Re}(u) \text{Re}(v) (2 + \beta^2)(7 + \beta^2).
\]

Putting the two parts of energy together, we have

\[
E_G = |u|^2 \beta^2 \Delta - \frac{2}{5} z t \text{Re}(u) \text{Re}(v) (2 + \beta^2)(7 + \beta^2) - \frac{36}{5} z|v|^2 (1 - \beta^2)^2 + \frac{1}{5} z|v|^2 V(\beta^2),
\]

where $0 \leq \beta^2 \leq 1$ is imposed. Clearly, for the energy to be the lowest, both $u$ and $v$ must be chosen real and positive, and we shall assume so in the below.

We can eliminate $u$ by Eq. (12), so that $E_G$ becomes a function of $v$ and $\beta^2$ only. In the SLC phase, the minimum of $E_G$ will be reached at the point where the first order derivatives with respect to $v$ and $\beta^2$ both vanish. These
conditions can be explicitly written down as:

\[
0 = \frac{1}{v} \frac{\partial \mathcal{E}_G}{\partial v} = -\frac{4}{5}(2 + \beta^2)(7 + \beta^2)\beta^2 \Delta + \frac{2}{5} z v (\beta^2) - \frac{72}{5} z t (1 - \beta^2) \beta^2 \\
- z t \left[ \frac{2}{5} \left( \frac{u}{v} \right)^2 (2 + \beta^2)(7 + \beta^2) - \frac{4}{25} \left( \frac{v}{u} \right)^2 (2 + \beta^2)^2 (7 + \beta^2)^2 \right],
\]

\[
0 = \frac{1}{u^2} \frac{\partial \mathcal{E}_G}{\partial (\beta^2)} = \Delta - \frac{2}{5} z t \left( \frac{v}{u} \right) (9 + 2 \beta^2) + \frac{1}{5} z \left( \frac{v}{u} \right)^2 \left[ \frac{\partial V(\beta^2)}{\partial (\beta^2)} - 2 (9 \beta^2 + 2 \beta^4) \Delta - 36 t (1 - 2 \beta^2) \right].
\]

In this way, we have expressed the conditions in terms of \( v/u \) and \( \beta^2 \). Especially, exactly on the phase boundaries between SLC and Mott insulators, the above conditions should be satisfied at \( \beta^2 = 0 \) or \( \beta^2 = 1 \), which corresponds to a dimer MI state or a trimer MI state. For \( \beta^2 = 0 \), the conditions become:

\[
\Delta - \frac{18}{5} z t \left( \frac{v}{u} \right) + \frac{1}{5} z \left( \frac{v}{u} \right)^2 (16 E_{42} - 7 E_{32} + 21 E_{22} - 12 E_{12}) - \frac{36}{5} z t \left( \frac{v}{u} \right)^2 = 0.
\]

For \( \beta^2 = 1 \), the conditions are similar:

\[
\Delta - \frac{22}{5} z t \left( \frac{v}{u} \right) + \frac{1}{5} z \left( \frac{v}{u} \right)^2 (32 E_{42} - 21 E_{32} + 27 E_{22} - 16 E_{12} - 22 \Delta) + \frac{36}{5} z t \left( \frac{v}{u} \right)^2 = 0.
\]

Eqs. (19) and (20) gives the phase boundary curves separating the SLC phase and the MI phases. When solving the equations, one should take the positive root of \( v/u \) to get a physical result. In the limit \( |t/E_a| \ll 1 \), one find in both cases \( v/u \propto t/E_a \), so the phase boundaries take the limiting form:

\[
\Delta + a_\pm \frac{z t^2}{E_a} = \pm b_\pm \frac{z t^3}{E_a},
\]

where \( a_\pm \) and \( b_\pm \) are coefficients depending on \( U_{2J} \) only. \( \Delta \) can be replaced by \( \mu_0 - \mu \).

Particularly, for \( U_4 = 3 U_2 = 30 U_0 \) and \( z = 4 \), the phase boundaries are shown in Fig. 2. In the SLC regime, one can verify that the global minimum of the variational energy \( \mathcal{E}_G \) is reached at \( 0 < \beta^2 < 1 \), which indicates that an SLC state is achieved.

**Determination of the phase boundary of spinor BEC**

The phase boundary between Mott insulator and spinor BEC is obtained based on the Gutzwiller variational wave function method used in many previous studies. We first consider the transition from a dimer MI to a spinor BEC. The method proposes the following direct product wave function:

\[
|\varphi\rangle = \prod_i \left( \sqrt{1 - |\eta|^2 - |\xi|^2} |2, 0, 0\rangle_i + \eta \sum_m \varphi_m |3, 2, m\rangle_i + \xi^* \sum_m (-1)^m \varphi^*_m |1, 2, -m\rangle_i \right),
\]

where \( \varphi \) is a normalized spinor that characterizes the spinor BEC phase. The energy expectation of this wave function can be easily derived as:

\[
\mathcal{E}_{\text{spinor}} = |\eta|^2 E_{32} + |\xi|^2 E_{12} - z t (1 - |\eta|^2 - |\xi|^2) \left| \sqrt{\frac{7}{5} \eta} + \sqrt{\frac{2}{5} \xi} \right|^2 \\
= (\eta^*, \xi^*) \begin{pmatrix} E_{32} - \frac{z}{2} t \\ -\frac{\sqrt{7} \xi}{2} t \end{pmatrix} \begin{pmatrix} \eta \\ \xi \end{pmatrix} + \text{higher order terms},
\]

where \( E_{lm} \) is given in Eq. (11). When the quadratic term \((\eta^*, \xi^*)^T M(\eta, \xi)^T \) become non-positive, where \( M \) stands for the \( 2 \times 2 \) matrix in the above, the system falls into a spinor BEC phase. So the phase boundary is simply determined.
by the condition $\det M = 0$. Similarly we can obtain the phase boundary between the trimer MI and the spinor BEC phase. The phase boundary between SLC and spinor BEC can then be obtained via an interpolation.

However, this method is only accurate to the first order of $t/E_a$. With higher order corrections, the phase boundary should be further modified, which we shall not do here. On the other hand, the above calculation for the SLC phase is done up to the third order of $t/E_a$, so the two results may not match very well. Therefore, we add a higher order correction to the spinor BEC phase boundary, so that the triple point of the dimer MI, trimer MI and the spinor BEC calculated using the Gutzwiller method is located inside the SLC phase, as it should be. The resulting phase diagram is shown in Fig. 2. We note that according to Ref. [4–6], the spinor BEC phase in the case $U_4 = 3U_2 = 30U_0$ should be a spin 2 nematic phase.