Plaquette valence bond ordering in a $J_1-J_2$ Heisenberg antiferromagnet on a honeycomb lattice

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Abstract
We study an $S = 1/2$ Heisenberg model on the honeycomb lattice with first and second neighbor antiferromagnetic exchange ($J_1-J_2$ model), employing exact diagonalization in both the $S_z = 0$ basis and nearest neighbor singlet valence bond (NNVB) basis. We find that for $0.2 < J_2/J_1 < 0.3$, the NNVB basis gives a proper description of the ground state in comparison with the exact results. By analyzing the dimer–dimer as well as the plaquette–plaquette correlations and also defining appropriate structure factors, we investigate possible symmetry breaking states as the candidates for the ground state in the frustrated region. We provide a body of evidence in favor of plaquette valence bond ordering for $0.2 < J_2/J_1 < 0.3$. By further increasing the ratio $J_2/J_1$, this state undergoes a transition to the staggered dimerized state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Quantum spin liquid (QSL) is a nonmagnetic state of correlated matter for which there is no broken symmetry in the spin part of the ground state wavefunction. Hence the local magnetic moments remain disordered down to absolute zero ($T = 0$) [1]. The quantum ground state for QSL can be expressed as the superposition of many different configurations, such as linear combinations of the short range singlet valence bonds. This state is called the resonating valence bond (RVB), originally proposed by Fazekas and Anderson as the ground state of the Heisenberg model on the triangular lattice [2]. The singlet bonds in the RVB state can be considered as preformed Cooper pairs, which under suitable conditions (i.e. hole doping) may coherently propagate throughout the system, hence giving rise to superconductivity [3].

Many strongly correlated systems are well described by a Hubbard Hamiltonian whose ground state for large on-site Coulomb interaction is the Mott insulating state. In this state the electrons are localized on the atoms, nevertheless charge fluctuations induce an antiferromagnetic (AF) exchange interaction between the spins of the electrons. Hence, the AF Heisenberg model is an effective Hamiltonian for describing the low energy excitations of the Mott insulators [4]. It has been proved that in one dimension, the ground state of the Heisenberg model is a gapless (critical) spin liquid for a $S = 1/2$-chain, while it is a gapped spin liquid for an $S = 1$-chain [5]. Finding the realizations of QSL in two and three dimensions has been the subject of much research in recent years [1]. Quantum fluctuations as well as frustration may destroy the long range magnetic order in spin systems. When a spin system is frustrated, it cannot find a spin configuration to fully satisfy the interaction between each pair of spins. There are two mechanisms for frustration: (i) geometrical frustration, where the lattice geometry is such that it is not possible to minimize the interaction energy of all bonds at the same time, e.g. in a triangular or Kagomé lattice in two dimensions and a pyrochlore lattice in three dimensions [6]; (ii) when there are several competing exchange interactions, such as competition between first
and second neighboring AF exchange interactions \((J_1-J_2)\) model. Since the quantum fluctuations are larger in two dimensions, many attempts to find QSL have focused on the quasi-two-dimensional (quasi-2D) frustrated spin systems with \(S = 1/2\) \([7]\).

2D Heisenberg antiferromagnets, apart from in their own right \([4]\), have received intensive attention in the context of layered high-\(T_c\) superconducting (HTSC) material \([3]\). The ground state of the \(S = 1/2\) Heisenberg model with AF nearest neighbor (NN) exchange coupling on 2D bipartite lattices has been shown to be Néel ordered \([8–14]\). Addition of next nearest neighbor (NNN) AF interactions frustrates the system and gradually destroys the (Néel) order. Since AF exchange interaction encourages the singlet formation, the quantum ground state of the AF Heisenberg model can be expressed in terms of a complete valence bond (VB) basis which represents a total spin singlet state \([15]\).

The \(J_1-J_2\) AF Heisenberg model on a square lattice has been extensively studied and various VB states have been proposed to describe its disorder regime \([16]\). One example of such a quantum state is the nearest neighbor RVB representing a spin liquid, which breaks neither translational nor rotational symmetries. However, in the highly frustrated regime where the ground state is classically disordered and the \(SU(2)\) symmetry of the Hamiltonian is restored, there is no theorem to prevent breaking of the lattice translational symmetry. Therefore, in spite of the earlier proposal of states with no symmetry breaking \([17]\), states which break translational symmetry were proposed \([18–20]\). One example is the staggered dimerized state which breaks translational and rotational symmetries of the lattice. Another candidate that has been proposed recently for some lattices is plaquette RVB (PRVB) wavefunctions in which the resonance of VBs is limited to one plaquette \([21–25]\). The PRVB state breaks the translational symmetry, while preserving the rotational symmetry of the lattice.

Recent fabrication of a graphene monolayer and also magnetic compounds with quasi-2D honeycomb structure, has brought the honeycomb lattice to the attention of physicists from both experimental and theoretical points of view. A honeycomb lattice does have a coordination number equal to three, which is a minimum among 2D lattices. In the case of the Heisenberg model on a honeycomb lattice, the small number of neighboring interactions enhances the quantum fluctuations and therefore seems to be a promising system to explore spin liquid states. Honeycomb lattice is a bipartite lattice composed of two interlacing triangular sublattices (figure 1). The unit cell of this non-Bravais lattice contains two sites and the lattice is constructed by two lattice vectors of the triangular Bravais lattice. The non-Bravais character of the lattice results in more exotic aspects that cannot be seen in a square lattice or the other Bravais lattices \([26]\).

As some realizations of Heisenberg magnets on the honeycomb lattice, one can name recently discovered compounds such as InCu\(_2\)NO\(_3\) \([28]\) and Na\(_3\)Cu\(_2\)SbO\(_6\) \([27]\) in which the Cu\(^{2+}\) ions in the copper-oxide layers form a 2D \(S = 1/2\) Heisenberg antiferromagnet on a honeycomb lattice, Bi\(_3\)Mn\(_4\)O\(_{12}\)(NO\(_3\)) (BMNO) in which the Mn\(^{3+}\) ions with

![Figure 1. The bipartite honeycomb lattice. Two sublattices are marked by black and white circles. Nearest neighbor lattice points are connected with solid lines and next to nearest neighbor lattice points are connected with dashed lines. Red arrows show the two primitive lattice vectors.](image-url)
Figure 2. Three-fold degeneracy of the staggered dimerized wavefunction on a honeycomb lattice.

Figure 3. Three-fold degeneracy of the plaquette valence bond wavefunction on a honeycomb lattice.

Figure 4. Three-fold degeneracy of the wavefunction proposed by Read and Sachdev on a honeycomb lattice.

2. Model Hamiltonian and its ground state candidates

The $J_1$–$J_2$ AF Heisenberg Hamiltonian is defined by,

$$
H = J_1 \sum_{\langle i,j \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} S_i \cdot S_j,
$$

(1)

in which $J_1 > 0$ and $J_2 > 0$ are AF exchange interactions between first and second neighboring spins, respectively. The first sum is limited to NN sites, while the second sum runs over the NNN lattice sites. Since the square lattice is connected with high $T_c$ superconducting materials, studies of frustrated phases of spin models have been usually limited to this lattice. Recently discovered magnetic materials with underlying honeycomb geometry are our motivation to study the above model on the honeycomb lattice.

Using the effective action approach on the frustrated Heisenberg antiferromagnet in a 2D system, Einarsson et al proved that the $S = 1/2$ disorder ground state on the honeycomb lattice is three-fold degenerate [33]. Fouet et al [34] provided some evidence for a staggered dimerized (SD) state for $S = 1/2$ at $J_2/J_1 = 0.4$. Such a state breaks the rotational lattice symmetry ($C_3$), while preserving its translational symmetry (figure 2). They also speculated that the spin liquid phase and PRVB phases can be stabilized for some range of $J_2/J_1$ (figure 3). The PRVB phase breaks the translational symmetry, but preserves the rotational symmetry of the lattice. Alternatively, Read and Sachdev [35], using the large $N$ expansion method, proposed another ground state wavefunction which breaks both the translational and the rotational symmetries of the lattice (figure 4). By transforming the spin system to a non-linear sigma model and based on renormalization group treatment of this model, Takano found a disordered spin gapped phase for the frustrated Heisenberg model on a honeycomb lattice [36]. Such a spin gapped phase has also been found by Cabra et al, using linear spin-wave and the Schwinger boson methods [37].

In the classical limit (large spins), it has been shown that the ground state of the above model is Néel ordered for $J_2/J_1 < 1/6$ while for $J_2/J_1 > 1/6$ the ground state consists of an infinitely degenerate set of spiral states characterized by spiral wavevectors $q$ [38]. Okumura et al [39], using a combination of low temperature expansion and Monte Carlo simulation, showed that thermal fluctuations can lift the huge degeneracy of the ground state, leading to a state with broken $C_3$ symmetry of the honeycomb lattice. According to their finding, in the vicinity of the Néel phase boundary, the energy scale associated with the thermal order-by-disorder becomes so small that exotic spin liquid behavior, such as ring liquid or pancake liquid can emerge. Mulder et al argued that taking the quantum fluctuations into account, some specific wavevectors in this manifold are picked as the ground state—a manifestation of the order-by-disorder mechanism. They found for $S = 1/2$ that quantum fluctuations are strong enough to destroy the spiral order and stabilize the valence bond solid with staggered ordering [40]. Our aim in this paper is to study the ground state of model (1) using exact diagonalization in both the $S_z$ and nearest neighbor valence bond (NNVB) basis.
3. Diagonalization in NNVB basis

The valence bond states are a subset of the $S_z = 0$ basis with total spin magnitude $S^2$ equal to zero. In this section we show that the ground state of the $J_1$–$J_2$ Heisenberg model in the frustrated regime, where there is no long range order, can be very well approximated in terms of states in NNVB subspace.

Let us expand the ground state wavefunction in terms of NNVB states as

$$|\psi_0\rangle = \sum_\alpha a(\alpha_0)|\alpha_0\rangle,$$

where $|\alpha_0\rangle$ denotes all possible configurations $\alpha$ of NNVBs:

$$|\alpha_0\rangle = \prod_{(i,j)\in\alpha} \left(i \cdot J_1 - j \cdot J_1\right).$$

First, we have to enumerate the basis $|\alpha_0\rangle$ to construct a numerical representation of the Hamiltonian matrix in this basis. To determine the basis, the exact Pfaffian representation of the RVB wavefunction is employed [41]. In this method one expresses the RVB wavefunction as the Pfaffian of an antisymmetric matrix whose dimension is equal to the number of lattice points. The NNVB basis is much smaller than the whole $S_z = 0$ basis, so that the Hamiltonian matrix can be fully diagonalized with standard library routines. Note that since the NNVB states $(|\alpha_0\rangle)$ are not orthonormal, one needs to solve the generalized eigenvalue problem

$$\det[\mathcal{H} - E\mathcal{O}] = 0,$$

where $\mathcal{O} = \langle \alpha_\beta | \alpha_\alpha \rangle$ denotes the overlap matrix of the NNVB configurations.

In the upper panel of figure 5 we have compared ground state energies obtained in the NNVB basis, and those obtained by numerically exact diagonalization in the $S_z = 0$ basis versus $J_2/J_1$ for $N = 32$. In the middle panel we show the relative error in the ground state energy and the lower panel shows the overlap of the exact ground state wavefunction with the ground state obtained within the NNVB basis set. As can be seen in this figure, the agreement between the two sets of energies for $J_2/J_1 \in [0.2, 0.3]$ is remarkable. Since the NNVB basis is not complete, the large error obtained by the NNVB basis for $J_2/J_1 < 0.2$ and $J_2/J_1 > 0.3$ can be attributed to the fact that longer range valence bonds start to contribute. For $J_2/J_1 < 0.2$, where there is Néel order in the ground state, it was shown that long ranged VB states have a remarkable contribution in the ground state wavefunction [42]. Starting from $J_2/J_1 = 0$, the Néel order is destroyed by increasing the frustration strength up to $J_2/J_1 \approx 0.2$. At this point, the spin–spin correlations will become short ranged and the nature of the ground state can be accurately captured by NNVB wavefunctions. For $J_2/J_1 > 0.3$, the frustrating second neighbor AF exchange coupling $J_2$ induces singlet formation between next nearest neighbors which compete with NNVBs. Therefore in this region the NNVB basis is insufficient to capture the true ground state. Furthermore, upon increasing $J_2/J_1$ beyond 0.35, as will be shown shortly, the nearest neighbor singlets in the VB states (dimers) will start to become correlated.

The RVB wavefunction (QSL) is defined as a linear superposition of all possible VB configurations with the same amplitude. Thus it can be represented as:

$$|\text{RVB}\rangle = A \sum_\alpha |\alpha_0\rangle,$$

in which $A = (\sum_\alpha \langle \alpha_0 | \alpha_\alpha \rangle)^{-\frac{1}{2}}$ is the normalization coefficient. In order to get preliminary insight into the nature of the ground state obtained in the NNVB basis, we compare the distribution of the amplitudes of VB configurations in equation (2) to the uniform amplitude $A$ of the above RVB liquid state. For this purpose we define the ratio $w(\alpha_0) = \langle c_\alpha|c_0\rangle$, and look at the distribution of relative weights, $w$. If the ground state has the characteristics of a RVB spin liquid, this
distribution is expected to be sharply peaked around \( w = 1 \). In figure 6 we plot the probability distribution function (PDF) of the relative amplitudes \( w \) for \( J_2/J_1 = 0.2 \) and 0.4 in a cluster of \( N = 54 \) spins. As can be seen in this figure, for \( J_2/J_1 = 0.2 \) the PDF is narrower relative to \( J_2/J_1 = 0.4 \), which implies that the ground state for \( J_2/J_1 = 0.2 \) is more similar to the spin liquid state. The broader distribution of amplitudes for \( J_2/J_1 > 0.4 \), on the other hand, indicates significant deviation from QSL behavior, which can be considered as a sign of symmetry breaking. To investigate the effect of finite lattice geometry on the ground state, we compare PDFs of relative amplitudes for two cluster sizes \( N = 50 \) and 54, and \( J_2/J_1 = 0.2 \) and 0.35. These are shown in the two top panels of figure 7. It can be easily seen that, for the lattice size \( N = 50 \), the PDFs are more symmetric than \( N = 54 \). This can be attributed to the fact that, in contrast to the cluster with \( N = 50 \) lattice points, the plaquette wavefunction can be fitted to the cluster with \( N = 54 \) subject to the periodic boundary condition. Therefore the symmetry breaking toward plaquette formation is more pronounced for \( N = 54 \). This signals a tendency for plaquette formation, provided it is compatible with the lattice geometry. Moreover for \( N = 54 \), increasing the value of \( J_2 \) leads to the emergence of a second peak at the right tail of the PDF. The average of relative amplitudes of VB configurations taking part in the plaquette wavefunction turns out to be 1.56. Interestingly, the position of the second peak is quite close to this value. Therefore, the second peak can be attributed to the amplification of plaquette character in the ground state, as a result of increasing the second neighbor exchange interaction. To quantify the variations of PDF (\( p(w) \)) versus \( J_2/J_1 \), we compute its width given by the standard deviation (\( \sigma = \langle (w - \langle w \rangle)^2 \rangle^{1/2} \)) and also its skewness defined by \( \langle (w - \langle w \rangle)^3 \rangle / \sigma^3 \). Panel (c) of figure 7 is a plot of width versus \( J_2/J_1 \) for \( N = 54 \), showing that the width of the PDF increases monotonically from \( J_2/J_1 = 0.2 \) to 0.4. The panel (d) in this figure, represents the rise of PDF skewness for \( N = 54 \) in terms of \( J_2/J_1 \), indicating that by increasing \( J_2 \) the distribution functions for this size get more and more asymmetric, while for \( N = 50 \) skewness does not change remarkably. This suggests that the skewness can be considered as a heuristic indication of possible symmetry breaking. In summary, since the widths of PDFs considered here are finite for the interval \( 0.2 \lesssim J_2/J_1 \lesssim 0.35 \), the above arguments suggest that the ground state of the \( J_1-J_2 \) model in this interval is not a perfect QSL state. A more precise understanding of the ground state properties requires us to study the correlation between dimers. This will be done in section 4.

4. Exact dimer–dimer correlations

In this section, by employing exact diagonalization, we obtain the ground state in the \( S_z = 0 \) basis. Using the exact
wavefunction of the ground state, we calculate the correlation between dimers for $0.2 \lesssim J_2/J_1 \lesssim 0.5$. The dimer–dimer correlation is defined by

$$C(\alpha, \alpha') = 4\langle (S_i \cdot S_j)(S_k \cdot S_l) \rangle - \langle (S_i \cdot S_j) \rangle^2,$$  

where $\alpha' = (k, l)$, and $\alpha = (i, j)$ is the reference bond relative to which the correlations are calculated. We define the permutation operator by

$$P_{kl} = 2(S_i \cdot S_j) + \frac{1}{2},$$  

in terms of which equation (5) can be alternatively expressed as

$$C(\alpha, \alpha') = \langle P_{kl} P_{\alpha'} \rangle - \langle P_{\alpha'} \rangle \langle P_{kl} \rangle.$$  

In Table 1 quantities $C(\alpha, \alpha')$ for fixed $\alpha$ and $\alpha' = \beta, \gamma, \delta$ (figure 8) are shown for three trial wavefunctions $\psi_{\text{SD}}, \psi_{\text{PL}}$ and $\psi_{\text{RS}}$, where RS, SD and PL stands for Read–Sachdev, staggered dimerized and plaquette states, respectively. The expectation values of the operator $\langle P_{\alpha'} \rangle$ for each of the three degenerate SD and RS states is $-1$ if bond $\alpha'$ is occupied by a dimer, and $+1/2$, otherwise. $\langle P_{\alpha'} \rangle_{\text{avg}}$ in Table 1 is obtained by averaging over three degenerate states corresponding to SD and RS trial wavefunction. For the PL trial state, since the three degenerate configurations are not orthogonal in the thermodynamic limit, the averaging is not valid and we compute $C(\alpha, \alpha')$ numerically by a finite size scaling method. Figure 9 gives a graphical representation of the correlations obtained in this way. Red and blue links (color in electronic form) denote positive and negative correlations, and their thickness is proportional to the magnitude of correlations with the reference bond $\alpha$ of figure 8. The reference bond $\alpha$ is denoted by a double line in figure 9. It can be seen in this figure that the patterns for the sign of correlations in PL and RS states are identical, except for their magnitudes. Specifically, in the PL state, the magnitudes of correlations between the dimers, which belong to the same hexagon as the reference bond, are stronger than the rest of the dimers, but in the RS state all dimers have identical correlation with respect to the reference bond.

In Figures 10 and 11, we have shown the exact diagonalization results for the dimer–dimer correlation functions at $J_2/J_1 = 0.3$ and $J_2/J_1 = 0.4$, respectively, for a lattice with $N = 32$ sites, subject to periodic boundary conditions. Note that in order to implement symmetries of an infinite lattice on finite size systems, the size $N$ is limited to specific numbers $N = 24, 32, 42, 50, 54, \ldots$. Since the dimension of Hilbert space grows exponentially with $N$, the exact diagonalization in the whole $S_z = 0$ subspace is not feasible and hence for $N > 32$ we carried out the calculations in the NNVB basis. The correlations are computed with respect

Table 1. $(P_\beta P_\gamma) - (P_\alpha)^2$ for $\alpha$ fixed and $\alpha' = \beta, \gamma, \delta$ (figure 8). The three indices 1–3 refer to three degenerate states (compare with figures 2–4) which become orthogonal to each other in the thermodynamic limit for pure SD and RS states. The subscript avg denotes the average over these three possible degeneracies. Since the three degenerate PL states are not orthogonal to each other in the thermodynamic limit, in this case the correlations have been extracted from finite size scaling of the numerical data. Digits in parentheses denote errors in the last digit.

| $\langle P_{\alpha} \rangle_{\text{avg}}$ | $\psi_{\text{SD}}$ | $\psi_{\text{PL}}$ | $\psi_{\text{RS}}$ |
|--------------------------------------|------------------|------------------|------------------|
| $\alpha'$ | $\beta$ | $\gamma$ | $\delta$ | $\beta$ | $\gamma$ | $\delta$ | $\beta$ | $\gamma$ | $\delta$ |
| $(P_{\alpha} P_{\beta})_1$ | +1/4 | +1/4 | +1/4 | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-1/2$ | $1$ | $-1/2$ | $+1/4$ | $-1/2$ | $1$ |
| $(P_{\alpha} P_{\gamma})_2$ | +1/4 | +1/4 | $-1/2$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ | $+$ | $+1/4$ | $+1/4$ | $-1/2$ | $1$ | $-1/2$ | $+1/4$ |
| $(P_{\alpha} P_{\delta})_3$ | +1 | +1 | $-1/2$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-1/2$ | $+1/4$ | $+1/4$ | $+1/4$ | $+1/4$ | $1/4$ |
| $(P_{\alpha} P_{\alpha'})_{\text{avg}}$ | 1/2 | 1/2 | $-1/4$ | $-0.090(5)$ | $0.170(8)$ | $-0.090(5)$ | $0.170(8)$ | $-0.090(5)$ | $0.170(8)$ | $-1/4$ | $+1/2$ | $-1/4$ | $+1/2$ | $-1/4$ | $+1/2$ | $+1/2$ |

**Figure 8.** The reference bond $\alpha$ and three independent bonds $\beta, \gamma, \delta$. 

**Figure 9.** Snapshots of correlations corresponding from left to right to (a) RS, (b) PL and (c) SD trial states. Red and blue links correspond to positive and negative correlations with respect to reference bond $\alpha$ which has been denoted by a double line.
Figure 10. The dimer–dimer correlation for a honeycomb lattice with periodic boundary conditions at $J_2 = 0.3$. Red (blue) lines denote positive (negative) correlation. The thickness of the lines is proportional to the magnitude of correlations. The system size is $N = 32$.

to the middle bond indicated by double lines. Red bonds denote positive correlations, while the blue ones indicate negative correlations. The thicknesses of bonds are proportional to the magnitude of correlations. As can be seen in figure 10, for $J_2/J_1 = 0.3$, the correlations are decaying with distance (measured with respect to the central bond). Comparing this correlation map with figure 9(b) shows remarkable similarity to the snapshot corresponding to PL ordering.

The dimer–dimer correlation pattern at $J_2/J_1 = 0.4$ shown in figure 11 is entirely different. First the dimer–dimer correlations do not appreciably decay over the maximum distance displayed in the figure. Second, one can easily distinguish a staggered ordering pattern by noting that correlations between bonds parallel to the reference dimer are positive, while others are negatively correlated with the reference dimer. Comparing with figure 9(c), this correlation snapshot obviously suggests a staggered dimerized state at $J_2/J_1 = 0.4$. This is in agreement with the previous study of Fouet et al [34]. However, Fouet et al speculated that at $J_2/J_1 = 0.3$ the correlation pattern resembles an RS state. Based on a qualitative symmetry consideration of short range dimer–dimer correlations, Fouet et al proposed the possibility of a crystal of hexagon plaquettes as a candidate for the ground state in the $0.3 < J_2/J_1 < 0.35$ range [34]. In the following we demonstrate that for $0.2 \lesssim J_2/J_1 \lesssim 0.3$, the dominant correlations are of PL type, rather than RS.

For quantitative characterization of the nature of the VB crystalline state, we define the following structure factor:

$$S_\lambda = \sum_\alpha \varepsilon_\lambda(\alpha') C(\alpha, \alpha'),$$

where $C(\alpha, \alpha')$ is given by equation (7) and $\varepsilon_\lambda(\alpha')$ is the phase factor, appropriately defined for each of the three states $\lambda \equiv \text{SD, PL, RS} [24]$. The phase factors $\varepsilon_{\text{SD}}, \varepsilon_{\text{PL}}$ and $\varepsilon_{\text{RS}}$ are shown in figure 12. Since the signs of dimer–dimer correlations for PL and RS states are the same, their phase factors must be equal. The scaling behavior of $S_\lambda$ for a lattice with $N$ sites and $N_b$ bonds is given by

$$\frac{S_\lambda}{N_b} = C_\lambda^N + \frac{A}{N}.$$  

Using the above phase factors and the correlations $C(\alpha, \alpha')$ given in table 1 we have calculated the corresponding $C_\lambda^N$ in table 2 for each of the three trial states $\psi_\lambda$. 

Table 1

| State | $C_\lambda^N$ |
|-------|--------------|
| SD    | $C_\text{SD}^N$ |
| PL    | $C_\text{PL}^N$ |
| RS    | $C_\text{RS}^N$ |

Table 2

| State | $C_\lambda^N$ |
|-------|--------------|
| SD    | $C_\text{SD}^N$ |
| PL    | $C_\text{PL}^N$ |
| RS    | $C_\text{RS}^N$ |

Figure 11. The dimer–dimer correlation for a honeycomb lattice with periodic boundary conditions at $J_2 = 0.4$. Red (blue) lines denote positive (negative) correlation. The thickness of the lines is proportional to the magnitude of correlations. The system size is $N = 32$.

Figure 12. Red and blue links correspond to $+1$, $-1$ phase factors, respectively, while the dashed links stand for 0. The reference dimer is identified by a double link. (a) The phase factor convention for PL and RS states. (b) Phase factors for the staggered dimerized state.
In figure 13 we have shown \( S_{\text{SD}} \) and \( S_{\text{PL}} \) versus \( J_2/J_1 \) for \( N = 24, 42, 54 \). Note that for \( N = 24 \), we have done exact diagonalization in the 5 site = 0 basis, while for \( N = 42, 54 \), the NNVB basis has been used. Note that the NNVB calculations are valid only in the region \( 0.2 < J_2/J_1 < 0.35 \). With these three sizes, we have performed finite size scaling according to equation (9) to obtain \( C_{\text{SD}}^\infty \) and \( C_{\text{PL}}^\infty \). Figures 13(a) and (b) show SD and PL structure factors, respectively, for various sizes. For values of \( J_2/J_1 \geq 0.35 \) we do not have reliable data for \( N = 42, 54 \). Hence we have not reported finite size scaling for these values of \( J_2/J_1 \). For \( 0.2 < J_2/J_1 < 0.35 \), the SD structure factor in (a) remains much smaller than \( C_{\text{SD}}^\infty = 1/4 \) (table 2) for all three sizes. On the other hand, the PL structure factor in (b) can be extrapolated to a finite value between 0.07 and 0.1 (empty squares) which are comparable with the exact value 0.125 of the pure PL state (table 2).

A sudden jump observed in figures 13(a) and (b) suggests the existence of a first order phase transition from the PL to the SD state as one increases \( J_2/J_1 \) beyond a certain value between 0.35 and 0.4. In panels (b) of figure 13 the average ratio of the structure factor (averaged over the range \( 0.2 < J_2/J_1 < 0.35 \)) to the corresponding \( C_{\text{SD}}^\infty \) is given by \( (S_{\text{PL}}/N_b)/C_{\text{PL}}^\infty \approx 0.66 \), while this ratio for the SD state in the same region is \( (S_{\text{SD}}/N_b)/C_{\text{SD}}^\infty \approx 0.08/0.375 \approx 0.21 \). Hence for \( 0.2 < J_2/J_1 < 0.35 \) we expect the ground state to be dominated by plaquette valence bond order.

In addition we calculated the exact value of \( \langle P_\nu \rangle \) as a function of \( J_2/J_1 \) for \( N = 24 \) sites. For \( J_2/J_1 \) from 0.2 to 0.35, the expectation value \( \langle P_\nu \rangle \) increases monotonically from −0.21 to −0.12 and shows a sudden jump to 0.001 for \( J_2/J_1 = 0.4 \). In view of the \( \approx 0.1 \) value for the expectation value of the permutation operator in the PL state (table 1), the negative values in the range \( 0.2 < J_2/J_1 < 0.35 \) can be considered as an extra support in favor of the plaquette valence bond solid in this regime. Guided by the above evidence for plaquette ordering in the region \( 0.2 < J_2/J_1 < 0.35 \), in section 5 we calculate the plaquette–plaquette correlation using the exact diagonalization method.

### 5. Plaquette order in the frustrated regime

A more direct tool to detect plaquette ordering in the frustrated regime is to investigate the plaquette–plaquette correlation defined by

\[
C(p, q) = \langle Q_p Q_q \rangle - \langle Q_p \rangle^2, \quad Q_p = \frac{1}{2} (\Pi_p + \Pi^{-1}_p),
\tag{10}
\]

where \( p, q \) stand for different plaquettes and \( \Pi (\Pi^{-1}) \) is the cyclic exchange operator which permutes six spins around a hexagon in a clockwise (counterclockwise) direction. This correlation function was introduced recently and has been used to investigate plaquette ordering in frustrated Heisenberg magnets on the checkerboard and square lattice [21–23, 25].

In figure 14(a) we have depicted the plaquette correlation in the PL state. Red (blue) circles indicate positive (negative) correlations, with the radii of circles being proportional to the magnitude of correlation. The reference plaquette is marked with a dashed circle. Figures 14(b) and (c) represent the plaquette correlation function obtained by exact diagonalization in the \( S_z = 0 \) basis for \( N = 24 \) sites at \( J_2/J_1 = 0.3, 0.5 \), respectively. Comparison of panels (b) and (c) of figure 14 with panel (a) indicates substantial PL ordering at \( J_2/J_1 = 0.3 \). It is remarkable to note that even the ratio of strengths of positive and negative correlations in (b) \( \sim 0.29:0.14 \) and (a) 0.35:0.13 agree with each other.

This ratio in (c) becomes 0.04:0.04 which significantly deviates from the corresponding value for a pure PL state (a). Figure 14(d) is the same as (b), for larger size \( N = 54 \) and \( J_2/J_1 = 0.3 \). As can be seen, for \( N = 54 \) too, a substantial plaquette correlation pattern can be observed. Moreover, for

### Table 2. Intensive structure factors in the thermodynamic limit for the three trial states.

| Trial state | \( \psi_{\text{SD}} \) | \( \psi_{\text{PL}} \) | \( \psi_{\text{RS}} \) |
|-------------|-----------------|-----------------|-----------------|
| \( C_{\text{SD}}^\infty \) | 1/4 | 0 | 0 |
| \( C_{\text{PL}}^\infty \) | 0 | 0.125(5) | 3/8 |

Figure 13. The structure factor computed for the lattices with \( N = 24 \) (diamond), \( N = 42 \) (triangle) and \( N = 54 \) (square). \( N_b \) stand for the number of dimers. Structure factors correspond to (a) the staggered dimerized state, (b) the plaquette state. In (b), an empty square with an error bar indicates extrapolation to infinite lattice size. (c) A finite size scaling according to equation (9) for PL structure factors and \( J_2/J_1 = 0.3 \). As can be seen for a specific value of \( J_2/J_1 \) between 0.35 and 0.4, there is a sudden increase for the SD structure factor, which is accompanied by a sudden decrease in the PL structure factor.
6. Conclusion

In summary, diagonalizations of a $J_1$–$J_2$ antiferromagnet Heisenberg Hamiltonian on a honeycomb lattice in both the $S_z = 0$ basis and NNVB basis show a striking agreement between these two approaches in the parameter range $0.2 < J_2/J_1 < 0.3$. Therefore, in this region the ground state can be well described in terms of the singlet bonds between the nearest neighbor spins. Analysis of the exact dimer–dimer correlations, structure factors and also plaquette–plaquette correlations, suggests the existence of a plaquette valence bond crystal in this range of couplings. In fact the emergence of such PL ordering can be attributed to the quantum fluctuations due to the tendency of second neighbors to form singlets. This study also reveals a phase transition from the plaquette ordered to the staggered dimerized state at a point in the interval $J_2/J_1 \in [0.35, 0.4]$. Similar results, regarding plaquette ordering on the square lattice, have been previously obtained for a $J_1$–$J_2$–$J_3$ Heisenberg antiferromagnet in its maximally frustrated region, $J_2 + J_3 \sim J_1/2$, and for $J_2 < J_3 < J_1$ [24]. Our results are in contrast with those obtained by QMC simulation of the Hubbard model in the intermediate interaction regime [32], in the sense that QMC results in an RVB liquid phase with no broken symmetry for this region. Meng et al have only calculated short range dimer–dimer correlation. Therefore this difference might be due to the fact that the geometry of finite clusters used in their simulation is not compatible with PL ordering. Based on the present study, we believe that it is necessary to consider lattice geometries compatible with the PL state and to calculate the plaquette–plaquette correlation for precise determination of the broken symmetries in the ground state.

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Table 3. Relative plaquette–plaquette correlations for hexagons at different distances from the reference hexagon.

| $C(i, 0)/C(0, 0)$ | $\psi_{PL}$ | $\psi_{RVB}$ | $\psi_{ED}$ |
|-------------------|-------------|-------------|-------------|
| $i = 1$           | 0.12        | -0.04       | -0.08       |
| $i = 2$           | 0.28        | 0.13        | 0.175       |
| $i = 3$           | -0.12       | -0.04       | -0.07       |
| $i = 4$           | -0.12       | -0.008      | -0.05       |
| $i = 5$           | 0.28        | 0.05        | 0.11        |

denoted by 1–5 in figure 14(d)) with respect to the reference one to which number 0 is assigned. In the last column of table 3 we have listed the relative correlations, defined by $C(i, 0)/C(0, 0)$ and obtained by exact diagonalization in the NNVB basis, and compared them with corresponding values for PL and RVB states given in the first and second columns, respectively. As can be seen, for the RVB state this quantity decays rapidly with distance from the reference hexagon, while the exact data do not show such a rapid decaying. This again is evidence in favor of the PL nature of the ground state.

![Figure 14. Red (blue) circles denote positive (negative) correlations. The radii of circles are proportional to the value of the plaquette–plaquette correlation. The reference plaquette is depicted by a black dashed line. (a) The plaquette–plaquette correlation map calculated for the PL trial state. The exact plaquette–plaquette correlation evaluated using exact diagonalization on a honeycomb lattice for (b) $J_2/J_1 = 0.3$ and (c) $J_2/J_1 = 0.5$. (d) The PL–PL correlation pattern for $N = 54$ and $J_2/J_1 = 0.3$.](image-url)
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