ORVB Mean-Field Calculation in the Tight-Binding Model with Anti-Ferromagnetic Exchange

Ling-Lie Chau* and Ding-Wei Huang†

* Department of Physics, University of California, Davis, CA 95616;
† Department of Physics, Chung Yuan Christian University, Chung-Li, Taiwan.

ABSTRACT

We give a mean-field calculation for the odd-resonating-valence-bond ORVB pairing scheme. We obtain interesting quasi-particle excitation energy $E_k$ as a function of momentum $k$. It is distinctively different from those of the $d_{x^2-y^2}$-wave, the anisotropic-s-wave, and the p-wave. It is a gapless theory for superconductivity with well defined Fermi surface. The ground state of the ORVB scheme is not an eigenstate of the parity or the time-reversal transformation, thus both symmetries are violated. Some of them are already manifested in $E_k \neq E_{-k}$. It is interesting to find out if such pairing order-parameter scheme exists in some materials in nature.
The discovery of high $T_c$ superconductivity\cite{1} led to an enormous interest in models with strong correlations, especially the Hubbard model\cite{2} with strong repulsion.\cite{3-5} In a previous paper\cite{6}, we pointed out the existence of extended local symmetries in the large-$U$ Hubbard model at half-filling as well as the anti-ferromagnetic exchange model, and proposed a new order-parameter scheme, the odd-resonating-valence-bond (ORVB) scheme. We later in Ref.\cite{7} showed that, besides the current popular $d_{x^2-y^2}$-wave order-parameter scheme, the ORVB scheme is another natural consistent solution to the rigorous constraints imposed on the system under the thermal equilibrium. (Earlier Zhang pointed out that the pure s-wave order-parameter scheme is not allowed.\cite{8})

In this paper, we report the result of a mean-field calculation for the ORVB pairing scheme. We obtain interesting quasi-particle excitation energy $E_k$ as a function of the momentum $k$. It is a gapless theory for superconductivity with well defined Fermi surface. They are distinctively different from those of the $d_{x^2-y^2}$-wave pairing, the anisotropic-s-wave pairing, the p-wave pairing, and many other pairing schemes.\cite{9} Our ORVB scheme can be tested in the angle-resolved-photo-emission-spectroscopy (ARPES) experiments, however the experiments must scan many key directions in the whole Brillouin zone. The ground state of the ORVB scheme is not an eigenstate of the parity or the time-reversal operator, thus both symmetries are violated. Some of these symmetry violation effects have already manifested in $E_k \neq E_{-k}$.

It is interesting to find out experimentally if such pairing order-parameter scheme exits in some materials in nature or if it is a scheme for some high $T_c$ superconductivity.

We start with the following mean-field Hamiltonian of the tight-binding model with anti-ferromagnetic exchange,

$$
\hat{H}_{\text{mean}}^{\text{ORB}} = t \sum_{(\mathbf{r},\mathbf{r}')} \langle \hat{c}_{\mathbf{r},\sigma}^\dagger \hat{c}_{\mathbf{r}',\sigma} + \text{h.c.} \rangle + \mu \sum_{\mathbf{r},\sigma} \hat{c}_{\mathbf{r},\sigma}^\dagger \hat{c}_{\mathbf{r},\sigma} \\
- \frac{J}{2} \sum_{(\mathbf{r},\mathbf{r}')} \{ \Delta_{\mathbf{r},\mathbf{r}'} \hat{\Delta}_{\mathbf{r},\mathbf{r}'}^\dagger + \Delta_{\mathbf{r},\mathbf{r}'}^* \hat{\Delta}_{\mathbf{r},\mathbf{r}'} + \chi_{\mathbf{r},\mathbf{r}'} \hat{\chi}_{\mathbf{r},\mathbf{r}'} + \chi_{\mathbf{r},\mathbf{r}'}^* \hat{\chi}_{\mathbf{r},\mathbf{r}'} \}, \quad (1)
$$
where
\[
\hat{\Delta}_{\mathbf{r},\mathbf{r}'} \equiv \hat{c}_{\mathbf{r},\uparrow} \hat{c}_{\mathbf{r}',\downarrow} - \hat{c}_{\mathbf{r},\downarrow} \hat{c}_{\mathbf{r}',\uparrow}, \quad \hat{\chi}_{\mathbf{r},\mathbf{r}'} \equiv \hat{c}_{\mathbf{r},\uparrow} \hat{c}_{\mathbf{r}',\uparrow} + \hat{c}_{\mathbf{r},\downarrow} \hat{c}_{\mathbf{r}',\downarrow}. \tag{2}
\]

These two operators are related by the SU(2) symmetry, which is the symmetry of the J-term or the symmetry of the anti-ferromagnetic exchange.\[^6\] In obtaining the mean-field Hamiltonian, we have used the ORVB order parameters: \(\Delta_{\mathbf{r},\mathbf{r}'} \equiv \langle \hat{\Delta}_{\mathbf{r},\mathbf{r}'} \rangle \equiv \text{Tr}(e^{\beta \hat{H}} \hat{\Delta}_{\mathbf{r},\mathbf{r}'})\), where \(\hat{H}\) is the Hamiltonian and \(\beta = (kT)^{-1}\). At temperature \(T = 0\), \(\langle \hat{\Delta}_{\mathbf{r},\mathbf{r}'} \rangle = 0\), i.e., the expectation value of the ground state; similarly for \(\chi_{\mathbf{r},\mathbf{r}'} \equiv \langle \hat{\chi}_{\mathbf{r},\mathbf{r}'} \rangle\).

The doping parameter \(\delta\) is defined by \(1 - \delta = N^{-2} \sum_{\mathbf{r},\sigma} \langle \hat{c}_{\mathbf{r},\sigma} \hat{c}_{\mathbf{r},\sigma} \rangle\). The ORVB order-parameters can be parameterized in the following way:
\[
\Delta_{\mathbf{r},\mathbf{r}'} = \delta_{\mathbf{r}',\mathbf{r}} e^{i\hat{\pi}_{\mathbf{r}}^x} \Delta e^{i\theta}, \tag{3}
\]
\[
\chi_{\mathbf{r},\mathbf{r}'} = \delta_{\mathbf{r}',\mathbf{r}} e^{i\hat{\pi}_{\mathbf{r}}^y} \chi e^{i\phi}, \tag{4}
\]
where the unit vector \(\mathbf{e} = \mathbf{e}_x\) or \(\mathbf{e}_y\). As shown in Ref.\[^7\], the rigorous constrains imposed by thermal equilibrium allow all these real order parameters, \(\Delta, \theta, \chi\) and \(\phi\) to be nonzero and unequal in different directions. For simplicity, as done in many other order parameter schemes, we choose them to be constants, independent of sites \(\mathbf{r}\). Notice that from the definitions of \(\hat{\Delta}_{\mathbf{r},\mathbf{r}'}\) and \(\hat{\chi}_{\mathbf{r},\mathbf{r}'}\) in Eq.(2), we have \(\Delta_{-\mathbf{r},-\mathbf{r}'} = -\Delta_{\mathbf{r},\mathbf{r}'}\) and \(\chi_{-\mathbf{r},-\mathbf{r}'} = (\chi_{\mathbf{r},\mathbf{r}'})^*\). In the case \(\Delta = 0\) but \(\chi \neq 0\) and \(\phi \neq 0\), the ORVB scheme becomes the flux phase scheme.\[^10\] However the main new features of the ORVB scheme come from \(\Delta \neq 0\) and the interplay between the two sets of order parameters given in Eqs. (3) and (4).

After the Fourier transformation, the Hamiltonian in momentum space becomes
\[
\hat{H}_{\text{mean}}^{\text{ORVB}} = \sum_{\mathbf{k},\sigma} \{2tC_{\mathbf{k}} + \mu - J\chi[\cos(k_x + \phi) + \cos(k_y + \phi)]\} \hat{c}_{\mathbf{k},\sigma}^\dagger \hat{c}_{\mathbf{k},\sigma}
- \sum_{\mathbf{k}} \{J \Delta S_{\mathbf{k}} [e^{-i(\theta + \frac{\pi}{2})} \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{\mathbf{k},\downarrow} + e^{i(\theta + \frac{\pi}{2})} \hat{c}_{\mathbf{k},\downarrow}^\dagger \hat{c}_{\mathbf{k},\uparrow}] \}, \tag{5}
\]
where $C_k \equiv \cos k_x + \cos k_y$ and $S_k \equiv \sin k_x + \sin k_y$. Obviously from Eq. (5) we see that the momenta of the electrons in the pairing are $k$ and $\pi - k$, in contrast to the $k$ and $-k$ of the BCS pairing.\[11\]

The Hamiltonian $\hat{H}_{\text{mean}}^\text{ORVB}$ can be diagonalized by the following Bogoliubov transformation $\hat{c}_{k,\downarrow} = u_k^* \hat{\gamma}_{k,\downarrow} + v_k \hat{\gamma}_{\pi-k,\uparrow}$ and $\hat{c}_{\pi-k,\uparrow} = -v_k^* \hat{\gamma}_{k,\downarrow} + u_k \hat{\gamma}_{\pi-k,\uparrow}$, where $\hat{\gamma}_{k,\sigma}$ and $\hat{\gamma}_{\pi-k,\sigma}$ are quasi-particle operators. Then the Hamiltonian becomes

$$\hat{H}_{\text{mean}}^\text{ORVB} = \Sigma_{k,\sigma}(E^\text{ORVB}_k \hat{\gamma}_{k,\sigma}^\dagger \hat{\gamma}_{k,\sigma} + E^0_k),$$

with the energy given by

$$E^\text{ORVB}_k = (2t - J\chi \cos \phi)C_k \pm \sqrt{|J\Delta S_k|^2 + [\mu + J\chi S_k \sin \phi]^2},$$

where $\pm$ are taken as the sign of $[\mu + J\chi S_k \sin \phi]$. Notice that when the order parameters become zero, $E^\text{ORVB}_k = \epsilon_k \equiv 2tC_k + \mu$.

The ORVB energy expression, Eq. (7), is quite different from those of the BCS-type of theories, $E^\text{BCS}_k = \pm \sqrt{\epsilon_k^2 + |J\Delta_k|^2}$, in which $\Delta_k = \Delta_s$ for the s-wave scheme (the original BCS order parameter); $\Delta_k = \Delta_d(cos k_x - cos k_y)$ for the $d_{x^2-y^2}$-wave scheme; $\Delta_k = \Delta_a[(cos k_x - cos k_y)^4 + \text{constant}]$ for the anisotropic s-wave scheme; (the sign in front of $E^\text{BCS}_k$ is that of $\epsilon_k$). Notice that when the order parameters are zero (at $T > T_c$), the ORVB scheme has the same energy expression, $E_k = \epsilon_k$, as the BCS-type of theories. When the order parameters becomes nonzero (at $T < T_c$), the BCS-type of theories gives energy discontinuity (gap) around $\epsilon_k = 0$. The ORVB scheme gives very different energy discontinuities, which we shall discuss later.

Notice that the momentum-factor associated with $\Delta$ in the $E^\text{ORVB}_k$ of Eq.(7) is $S_k$, a result of the pairing momentum being $\pi$. The momentum-factor associated with $\chi$ is $\cos(k_x + \phi) + \cos(k_y + \phi)$. It decomposes into $C_k \cos \phi$ and $S_k \sin \phi$; the former gives the term
outside the square root in Eq.(7), and the latter gives the term inside the square root in Eq.(7).

The ground state is defined by \( \hat{\gamma}_{k,\sigma}|0\) for \( E_k > 0 \) and \( \hat{\gamma}^\dagger_{k,\sigma}|0\) for \( E_k < 0 \). The quasi-particle operators \( \hat{\gamma}^\dagger_{k,\sigma} \) and \( \hat{\gamma}_{k,\sigma} \) are free fermions. \( \langle \hat{\gamma}^\dagger_{k,\sigma} \hat{\gamma}_{k,\sigma} \rangle \) are the only non-vanishing expectation-values. The requirement that the occupation number at a temperature \( T \) is given by the Fermi-Dirac distributions \( \langle \hat{\gamma}^\dagger_{k,\sigma} \hat{\gamma}_{k,\sigma} \rangle = [e^{\beta E_k} + 1]^{-1} \) imposes a set of consistent conditions upon the pairing parameters. After Fourier-transforming to momentum space and then Bogoliubov-transforming \( \hat{c} \) and \( \hat{c}^\dagger \) to \( \hat{\gamma} \) and \( \hat{\gamma}^\dagger \), we obtain the following four equations:

\[
\delta = N^{-2} \Sigma_k \left[ J\chi S_k \sin \phi + \mu \right] F_k X_k^{-1}, \quad (8)
\]

\[
2J\chi^2 \cos^2 \phi - 4t\chi \cos \phi = N^{-2} \Sigma_k (Y_k G_k), \quad (9)
\]

\[
2J (\Delta^2 + \chi^2 \sin^2 \phi) + \mu \delta = N^{-2} \Sigma_k (X_k F_k), \quad (10)
\]

\[
2J(\Delta^2 - \chi^2 \sin^2 \phi) - \mu \delta = N^{-2} \Sigma_k \{ [J\Delta S_k]^2 - [J\chi S_k \sin \phi + \mu]^2 \} F_k X_k^{-1}, \quad (11)
\]

where

\[
X_k \equiv \sqrt{[J\Delta S_k]^2 + [J\chi S_k \sin \phi + \mu]^2}, \quad (12a)
\]

\[
Y_k \equiv (J\chi \cos \phi - 2t\delta) C_k, \quad (12b)
\]

\[
F_k \equiv \sinh(\beta X_k) \left[ \cosh(\beta X_k) + \cosh(\beta Y_k) \right]^{-1}, \quad (12c)
\]

\[
G_k \equiv \sinh(\beta Y_k) \left[ \cosh(\beta X_k) + \cosh(\beta Y_k) \right]^{-1}. \quad (12d)
\]

For given temperature \( \beta \) and doping parameter \( \delta \), totally there are four equations, Eqs.(8), (9), (10), and (11), for the four unknowns \( \Delta, \chi, \phi, \) and \( \mu \). (Notice that the phase \( \theta \) does not appear in these equations.)
At $T = 0$, the temperature dependent factor $F_k = 1$ for $X_k > |Y_k|$ and $F_k = 0$ for $X_k < |Y_k|$; $G_k = 1$ for $Y_k > X_k$, $G_k = -1$ for $Y_k < -X_k$, and $G_k = 0$ for $|Y_k| < X_k$. Therefore Eqs.(8), (9), (10), and (11) are further simplified, which can be trivially obtained and we do not write them out explicitly.

We have analyzed Eqs.(8), (9), (10), and (11) numerically at small values of the doping parameter $\delta$ at various values of $T$. For a given small value of $\delta$, we find that the solution for these equations giving a small value of $\mu$ and Eq.(11) does not impose a strong independent condition from that of Eq.(10). [These can be understood by the fact that at $\delta = 0$ and $\mu = 0$ Eq.(11) reduces to Eq.(10) and Eq.(8) becomes an identity. However, our solution is different from the one exactly at half-filling, i.e. $\delta = 0$ and $\mu = 0$, where further degeneracy happens and gives a different solution.] Therefore for a small doping parameter $\delta$ only two of the parameters, $\chi^2cos^2\phi$ and $\Delta^2 + \chi^2sin^2\phi$ are determined, essentially by Eq.(9) and Eq.(10).

The approximate solutions we have obtained are the following: the critical temperature $T_c$ (that we define to be the temperature below which all the order parameters are nonzero) and the order parameters at $T = 0$ are all of the order of the interaction strength $J$; the order-parameters decrease as the doping parameter $\delta$ and/or as the temperature $T$ increases; $T_c$ decreases with the increasing value of the doping parameter $\delta$. For example, at $T = 0$ we find the approximate solution at $\delta \simeq 0.18$ ($t \simeq 0.18$): $\mu \simeq 0.08$, $\Delta^2 + \chi^2sin^2\phi \simeq 0.032$, and $\chi^2cos^2\phi \simeq 0$. From these discussions, we also see that our ORVB scheme contains the flux phase (i.e. $\chi \neq 0$ and $\Delta = 0$) and the case of $\chi = 0$ and $\Delta \neq 0$ as special cases. We shall see below that it is the general cases of both $\chi \neq 0$ and $\Delta \neq 0$ that give the interesting new physical phenomena.

With these solutions, we can calculate the quasi-particle excitation energy $E^{ORVB}_k$ of Eqs.(6) and (7). In Fig.1 we show the $E^{ORVB}_k$ distribution as function of $k$ for $\Delta \simeq 0.17$ and $\chi sin\phi \simeq -0.06$. Notice that the lattice lines of the Brillouin zones are no more the symmetry lines. We shall show later, this is a result from the violation of the parity as well
as the time reversal symmetries of our ORVB pairing scheme. The \( \chi \sin \phi \neq 0 \) gives a wall of discontinuity (gap) in the \( k \)-plane specified by \( S_k = -\mu / (J \chi \sin \phi) \), surrounding the centers at \((k_x, k_y) = (\pi / 2, \pi / 2)\), modulus \(2\pi\) in both \( k_x \) and \( k_y \). The magnitude of the discontinuity is \(|(2\mu \Delta) / (\chi \sin \phi)|\). Notice in Fig. 1 there are two lines of zero energy (gaplessness).\(^{[12]}\) The line of \( E_k = \epsilon_k \) is also symmetrically centered around \((k_x, k_y) = (\pi / 2, \pi / 2)\), which is not shown in the figure but can be easily seen from Eq.(7).

The quasi-particle excitation energy \( E_k \) distributions for the BCS-type theories are very different from that of the ORVB scheme we just presented. For BCS-type theories, the lattice lines of the Brillouin zones are the symmetry lines, a result of parity and time reversal symmetries. The anisotropic s-wave scheme is a finite-gap theory (i.e. \( E_k \neq 0 \) in the whole Brillouin zone) and the \( d_{x^2-y^2} \)-wave scheme has isolated four points of gaplessness. We shall mention at the end of the paper how these differences can be experimentally distinguished.

At \( T = 0 \), the occupation number in the quasi-particle space is

\[
\gamma_k \equiv < \hat{\gamma}^\dagger_k \hat{\gamma}^\downarrow_k + \hat{\gamma}^\dagger_k \hat{\gamma}^\uparrow_k > = 0 \quad \text{for} \quad E_k > 0 \quad \text{and} \quad n^\gamma_k = 2 \quad \text{for} \quad E_k < 0 .
\]

After Bogoliubov-transforming \( \hat{\gamma} \) and \( \hat{\gamma}^\dagger \) back to \( \hat{c} \) and \( \hat{c}^\dagger \), we obtain the occupation number in the electrons \( n^e_k \equiv < \hat{c}^\dagger_k \hat{c}^\downarrow_k + \hat{c}^\dagger_k \hat{c}^\uparrow_k > \), shown in Fig.2. These occupation number distributions are also very different from those of the BCS-type of theories.

We note that for every \( \chi \sin \phi < 0 \) solution, \( \chi \sin \phi = -0.06 \) in Fig.1, there is another equally allowed ORVB solution with \( \chi \sin \phi > 0 \) with the discontinuity center changed to \((k_x, k_y) = (-\pi / 2, -\pi / 2)\). The other characteristic are the same as those just discussed and presented for \( \chi \sin \phi < 0 \).

Besides the ORVB, there is another kind of solution to the thermal equilibrium constraint equations,\(^{[7]}\) which we call the \((\text{ORVB})'\) pairing scheme. In stead of Eqs.(3) and (4), we have

\[
\Delta_{r',r} = \delta_{r',r} e^{e_x \pi r} \Delta e^{i\theta} = -\delta_{r',r} e^{e_y \pi r} \Delta e^{i\theta} ,
\]

\( \Delta_{r',r} = \delta_{r',r} e^{e_x \pi r} \Delta e^{i\theta} \).
and $\Delta, \chi, \theta, \phi$ are real constants. The net result is that for $\chi \sin \phi < 0$, the discontinuity shifted to surround the centers at $(k_x, k_y) = (\pi/2, -\pi/2)$ modulus $2\pi$ in both $k_x$ and $k_y$; for $\chi \sin \phi > 0$, the discontinuity shifted to surround the centers at $(k_x, k_y) = (-\pi/2, \pi/2)$ modulus $2\pi$ in both $k_x$ and $k_y$.

Next, we discuss the intrinsic parity and time reversal symmetries. Both the $\Delta_{\mathbf{r}, \mathbf{r}'}$ and $\chi_{\mathbf{r}, \mathbf{r}'}$, Eqs.(3) and (4), violate the parity and the time reversal symmetries.

Under parity transformation $\hat{P}$, for any eigenstates of parity $|a> \text{ and } |b>$, the expectation value of any operator $\hat{O}$ has the identity $<a|\hat{O}|b>=<a|\hat{P}\hat{O}\hat{P}^{-1}|b>$. From the fact $\hat{P}\hat{c}_{\mathbf{r}, \sigma}\hat{P}^{-1}=\hat{c}_{-\mathbf{r}, \sigma}$ and $\hat{P}\hat{c}_{\mathbf{r}, \sigma}^{\dagger}\hat{P}^{-1}=\hat{c}_{-\mathbf{r}, \sigma}$, we obtain $\hat{P}\hat{\Delta}_{\mathbf{r}, \mathbf{r}'}\hat{P}^{-1}=\hat{\Delta}_{-\mathbf{r}', -\mathbf{r}}$ and $\hat{P}\hat{\chi}_{\mathbf{r}, \mathbf{r}'}\hat{P}^{-1}=\hat{\chi}_{-\mathbf{r}', -\mathbf{r}'}$ from the definitions of these operators in Eq.(4). If the eigenstates of Hamiltonian are eigenstates of the parity operator, the first relation implies $<\hat{\Delta}_{\mathbf{r}, \mathbf{r}'}>=<\hat{\Delta}_{-\mathbf{r}', -\mathbf{r}}>$; in which the right-hand-side (r.h.s.) is $\Delta_{\mathbf{r}, \mathbf{r}'}$, and the left-hand-side (l.h.s.) is $-\Delta_{\mathbf{r}, \mathbf{r}'}$, using Eqs.(3) and (4); thus must $\Delta_{\mathbf{r}, \mathbf{r}'} = 0$. The second relation implies $<\hat{\chi}_{\mathbf{r}, \mathbf{r}'}>=<\hat{\chi}_{-\mathbf{r}', -\mathbf{r}'}>$, in which the r.h.s. is $\chi_{\mathbf{r}, \mathbf{r}'}$ and the l.h.s. is $\chi_{\mathbf{r}, \mathbf{r}'}^{\ast}$; thus must $\chi_{\mathbf{r}, \mathbf{r}'} = \text{real}$, i.e., $\phi = 0$. Therefore, $\Delta \neq 0$ or the complexity of $\chi \sqrt[\phi]$, i.e., $\phi \neq 0$, implies that eigenstates of the Hamiltonian can not be the eigenstates of parity, i.e., parity is violated. Notice that this parity violation property is different from that of the p-wave pairing scheme, in which the ground state is an odd eigenstate of the parity transformation.$^{[9]}$

Under time reversal transformation $\hat{T}$, $\hat{T}|a>=|a_t>$ and $\hat{T}|b>=|b_t>$, the expectation value of any operator $\hat{O}$ has the identity $<a|\hat{O}|b>=<a|\hat{T}\hat{O}\hat{T}^{-1}|b>^\ast$. From the fact that $\hat{T}\hat{c}_{\mathbf{r}, \sigma}\hat{T}^{-1}=\hat{c}_{\mathbf{r}, -\sigma}$ and $\hat{T}\hat{c}_{\mathbf{r}, \sigma}^{\dagger}\hat{T}^{-1}=\hat{c}_{\mathbf{r}, -\sigma}^{\dagger}$, we obtain $\hat{T}\hat{\Delta}_{\mathbf{r}, \mathbf{r}'}\hat{T}^{-1}=\hat{\Delta}_{\mathbf{r}, \mathbf{r}'}$ and $\hat{T}\hat{\chi}_{\mathbf{r}, \mathbf{r}'}\hat{T}^{-1}=\hat{\chi}_{\mathbf{r}, \mathbf{r}'}$ from the definitions of these operators in Eq.(4). If the ground state is the eigenstate of time reversal $\hat{T}|0>=|0>$, $<0|\hat{\Delta}_{\mathbf{r}, \mathbf{r}'}|0>=<0|-\hat{\Delta}_{\mathbf{r}, \mathbf{r}'}|0>^\ast$ and $<0|\hat{\chi}_{\mathbf{r}, \mathbf{r}'}|0>=<0|\hat{\chi}_{\mathbf{r}, \mathbf{r}'}|0>^\ast$; which implies at temperature $T = 0$, $\Delta_{\mathbf{r}, \mathbf{r}'} = -\Delta_{\mathbf{r}, \mathbf{r}'}^{\ast}$ (i.e., $\Delta_{\mathbf{r}, \mathbf{r}'}$ is pure imaginary and
\[ \theta = \pi/2 \text{ and } \chi_{r,r'} = \chi_{r',r}^* \text{ (i.e., } \chi_{r,r'} \text{ is real and } \phi = 0, \pi \text{). Thus } \Delta \cos \theta \neq 0 \text{ or } \chi \sin \phi \neq 0 \text{ implies the violation of time reversal symmetry. (Note that } \chi e^{i\phi} = \chi, \text{ being real, is not an interesting order parameter, Since it only renormalizes the tight-binding term in the Hamiltonian.)} \]

If the ground state is an eigenstate of time reversal \( \hat{T}|0 \rangle = |0 \rangle \), following similar discussions as above, we can easily show that \( E_k \equiv <0|\hat{H}_{\text{mean}}|0 \rangle = E_{-k} \) from either the Hermiticity of the Hamiltonian, \( \hat{H}_{\text{mean}} = \hat{H}_{\text{mean}}^\dagger \), or \( \hat{T}\hat{H}_{\text{mean}}\hat{T}^\dagger = \hat{H}_{\text{mean}} \). Therefore, \( E_k \neq E_{-k} \) indicates that the ground state is not an eigenstate of time reversal. In our case, \( E_k \neq E_{-k} \) comes solely from the \( \chi \sin \phi \) term. If \( \chi \sin \phi = 0 \), our \( E_k = E_{-k} \) even if there is time-reversal violation from \( \Delta \cos \theta \neq 0 \); thus the time reversal violation effect from \( \Delta \cos \theta \) can not be observed in \( E_k \), since \( E_k \) is not sensitive to the phase of \( \Delta e^{i\theta} \).

Finally we point out some distinct features of the ORVB scheme that experiments can look for. In our ORVB scheme the wall of the energy discontinuity is off-centered in the Brillouin zone, centered in one of the quadrant of the Brillouin zone (see Fig. 1 and discussions in the text around the Eqs.(12) to (14)), in contrast to those of the \( d_{x^2-y^2} \)-wave and the anisotropic s-wave which are all centered symmetrically around the center of the Brillouin zone. It will be interesting to study such asymmetric distributions in experiments that can measure the energy discontinuities, like the ARPES experiments.[13] Due to complexity of the order parameters, in experiments that can measure the phases of order parameters (like the Josephson interference experiments) the ORVB scheme can give interference phase shifts different from \( \pi \), which is the only kind of interference phase shift the \( d_{x^2-y^2} \)-wave scheme can produce (due to the reality of its order parameter). We have also calculated the temperature dependence of the penetration depth. It increases with temperature faster than that from the \( d_{x^2-y^2} \)-wave case. (We shall publish our detail numerical results in a separate paper.)
To conclude, our ORVB scheme offers a pairing order parameter scheme for superconductivity very different from the current popular models, e.g., the $d_{x^2-y^2}$-wave scheme, the anisotropic s-wave scheme, and the p-wave scheme. It has interesting and distinct features that can be experimentally tested. Seeing the ORVB characteristics in some materials will certainly be very exciting.

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FIGURE CAPTIONS

Fig.1 The equal $E_k$, the quasi-particle energy, contour diagram as function of the momentum $k$ in the ORVB scheme with a small doping parameter $\delta$. For the values of parameters used and discussions, see the text. Notice that the wall of discontinuity (gap) is centered around the center of a quadrant of the Brillouin zone. Shown in the figure is the case of the center being at $(k_x, k_y) = (\pi/2, \pi/2)$. It is equally likely in the ORVB scheme that the center is at $(-\pi/2, \pi/2)$, $(\pi/2, -\pi/2)$, or $(-\pi/2, -\pi/2)$.

Fig.2 The three dimensional view of the electron density $n_k^e$ of the ORVB scheme.
REFERENCES

[1] J. G. Bednorz and K. A. Muller, Z. phys. B64 (1986) 189; M. K. Wu, J. R. Ashburn, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. 58 (1987) 908.

[2] J. Hubbard, Proc. Roy. Soc. A276 (1963) 238; P. W. Anderson, Science 235 (1987) 1196.

[3] G. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. 63 (1987) 973; V. Emery, Phys. Rev. Lett. 58 (1987) 2794; G. Kotliar, Phys. Rev. B37 (1988) 3664.

[4] S. Chakravarty, A. Sudbø, P. W. Anderson, and S. Strong, Science 261 (1993) 337.

[5] P. Monthoux and D. Pines, Phys. Rev. B47 (1993) 6069; D. Pines, Physica B199 and 200 (1994) 300; D. J. Scalapino, Physics Reports 250(1995) 329; J. R. Schrieffer, Sol. State Comm. 92 (1994) 129.

[6] L.-L. Chau, D.-W. Huang, and Y. Yu, Phys. Rev. Lett. 68 (1992) 2539.

[7] L.-L. Chau and D.-W. Huang, Constraints on Order Parameters and Correlation Functions of Systems in Thermal Equilibrium, submitted to Phys. Rev. B.

[8] S. C. Zhang, Phys. Rev. B42 (1990) 1012.

[9] For example the OPSP pairing scheme of R. T. Scalettar, R. R. P. Singh, and S. C. Zhang, Phys. Rev. Lett. 67 (1991) 370; the p-wave pairing scheme of A. V. Balatsky, E. Abraham, D. J. Scalapino, and J. R. Schrieffer, Physica B (1994) 363.

[10] I. Affleck and J. B. Marston, Phys. Rev. B37 (1988) 3774.

[11] J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. 108 (1957) 1175.

[12] As $\chi \sin \phi \to 0$, the discontinuity disappears and the energy $E_k$ becomes continuous:

$E_k^{ORVB} = (2t - J\chi \cos \phi) C_k + \sqrt{J^2 \Delta S_k^2 + \mu^2}$. As $|\chi \sin \phi|$ increases (remember that $\Delta^2 + \chi^2 \sin^2 \phi \simeq \text{constant}$), the area enclosed by the discontinuity enlarges and the discontinuity
along the boundary becomes smaller. When $|\chi \sin \phi|$ reaches its maximum ($\Delta = 0$), the spectrum becomes continuous again, $E^{ORVB}_k = (2t - J\chi \cos \phi)C_k + \mu + J\chi S_k \sin \phi$.

[13] It is impressive that the energy discontinuities can be measured at all. So far only partial regions of the Brillouin zone of Bi2212 has been scanned for the energy discontinuities by the ARPES experiments, see Z.-X. Shen, et al., Science 267 (1995) 343, and references therein.