Pair-Hopping Mechanism for Layered Superconductors

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We propose a possible charge fluctuation effect expected in layered superconducting materials. In the multireference density functional theory, relevant fluctuation channels for the Josephson coupling between superconducting layers include the interlayer pair hopping derived from the Coulomb repulsion. When interlayer single-electron tunneling processes are irrelevant in the Kohn-Sham electronic band structure calculation, the two-body effective interactions stabilize a superconducting phase. This state is also regarded as a valence-bond solid in a bulk electronic state. The hidden order parameters coexist with the superconducting order parameter when the charging effect of a layer is comparable to the pair hopping. Relevant material structures favorable for the pair-hopping mechanism are discussed.

KEYWORDS: superconductivity, iron pnictide, cuprate, density functional theory, Haldane gap

1. Introduction

The discovery of iron-pnictide superconductors gave us an interesting ground for testing theoretical approaches to analyze superconductivity. The first records of jump in the superconducting transition temperature in iron pnictides was observed in fluorine-doped LaFeAsO\textsubscript{1,2} when the discovery of fluorine-doped LaFePO\textsuperscript{3} fuelled a search for chemical trends in series of superconductors. Similar tests are also necessary to develop the theory of high-temperature superconductivity.

In the present standard of theoretical approaches to analyze superconductivity in materials science, we may apply the strong-coupling theory of superconductivity starting from estimation of electron-phonon coupling constants \textit{e.g.} by using the density-functional perturbation theory (DFPT).\textsuperscript{4} The applications of DFPT in high-temperature element superconductors\textsuperscript{5,6} suggest that the technique enables us to obtain a reasonable estimation of the transition temperature $T_c$ when the essential pairing mechanism is the electron-phonon-interaction-mediated stabilization of superconductivity. The method may also predict how to enhance the $T_c$ of compound superconductors. As an example of its application, I and my coworkers have shown that a possible positive jump in $T_c$ in CaSi\textsubscript{2} is expected at a high pressure when a structural phase transition to the AlB\textsubscript{2} structure takes place.\textsuperscript{7}

Recently, Jishi and Alahyaei have used this method to analyze the iron-based superconductors LiFeAs and NaFeAs.\textsuperscript{8} These 111 compounds may be ideal arsenides for the application of the strong-coupling theory, since clear superconducting transition temperatures of 18 K for
LiFeAs\textsuperscript{9,10} and 9 K for NaFeAs\textsuperscript{11} are reported under ambient condition without doping. Another experimental report on NaFeAs suggests a higher transition temperature of above 12 K without a clear indication of any coexisting magnetic ordering.\textsuperscript{12} Jishi and Alyahyaei unfortunately failed to obtain the transition temperature observed in experiments and concluded that the theory indicates a $T_c$ far below 1 K owing to insufficient electron-phonon coupling constants.

If one looks at a list of related materials,\textsuperscript{13} he or she might be motivated to perform another theoretical test in order to understand a chemical trend. The technique was applied to NaFeAs by A. Nakanishi and he considered a chemical trend by studying other two supposed material structures: NaCoAs and NaNiAs. Using the calculation results, Kusakabe and Nakanishi studied the electronic structures of these compounds to derive a chemical trend.\textsuperscript{14} A key to understand the trend could be found in the direction to substitute Fe with other transition-metal elements, since electronic bands around the Fermi level are known to originate from iron 3d orbitals in Fe\textsubscript{2}As\textsubscript{2} layers. However, note that there are only a few examples of nickel arsenides in the 1111 structure showing a finite $T_c$ of approximately 3 K.\textsuperscript{15,16} Fortunately, Nakanishi succeeded in observing the theoretical stability of the hypothetical compounds NaCoAs and NaNiAs, as well as NaFeAs, using first-principles structural optimization techniques\textsuperscript{17} with the generalized gradient approximation (GGA).\textsuperscript{18} He applied the strong-coupling theory and estimated the transition temperature within a standard approach. By means of first-principles lattice dynamics, the superconducting transition temperature was estimated to be approximately 0.034 K for NaFeAs, assuming that the system remained non-magnetic. An interesting finding was the increase in $T_c$ in the order of NaFeAs (0.034 K), NaCoAs (0.127 K), and NaNiAs (3.573 K), although there might remain systematic errors due to the limitation in the computation. However, this possible chemical trend is in inverse relation to the experimental finding of $T_c = 9$ K or $T_c > 12$ K for NaFeAs and the $T_c$ for Co and Ni compounds not higher than that for this iron arsenide.

As for the Kohn-Sham band structure on NaFeAs,\textsuperscript{14} the essential features around the Fermi level are rather similar to those of LiFeAs.\textsuperscript{19,20} The effective bands in a nonmagnetic solution are almost dispersionless along the c direction at approximately the Fermi level. Since electron and hole branches coexist and since DOS is reduced at approximately the Fermi level, we can conclude that the band structure has a semimetallic nature. That is, it shows strong two-dimensionality. Differently from LiFeAs, NaFeAs has two hole pockets. LiFeAs has three hole pockets on the two-dimensional plane including $\Gamma$-X-M lines in the first Brillouin zone. In addition, the two-dimensionality of the Fermi surface is much better for NaFeAs, and all of the pockets of NaFeAs except for one hole pocket around the $\Gamma$ point are rodlike.\textsuperscript{14}

A crude realization of the rigid band picture among three band structures for NaMAs (M=Fe, Co, Ni) has been reported. The correspondence of the major branches is clearly seen.
Thus, the band structures of NaCoAs and NaNiAs are approximately a result of heavy-electron doping in the band structure of NaFeAs. In many iron arsenides, we find a semimetallic two-dimensional band structure. Following this interpretation, we can understand the reason why the electronic density of states (DOS) at the Fermi energy increases when one considers the DOS's of NaCoAs and NaNiAs in comparison with that of NaFeAs. The Nakanishi data suggesting the increase in $T_c$ for NaCoAs and NaNiAs comes from the larger DOS together with the presence of more three-dimensional Fermi surfaces for these two compounds than for NaFeAs and the assumption of the electron-phonon-interaction-mediated superconductivity.

To go one step further, we can start analyzing the characteristic topology of Fermi surfaces. The chemical trend of the Kohn-Sham band structure in the series of NaFeAs, NaCoAs, and NaNiAs in $P4_{2}/nmn$ suggests that rodlike two-dimensional Fermi pockets appear only in NaFeAs, while more three-dimensional characters for Co and Ni compounds indeed enhance $T_c$ if the strong-coupling theory with the electron-phonon coupling is assumed to be applicable. This result as well as the theoretical data on the above known first-principles electronic structure calculations of 111 compounds leads us to a conclusion along the following line. An important ingredient tractable in the density functional theory (DFT) is charge fluctuation modes. If one of the modes becomes relevant on a two-dimensional Fermi surface, and if the fluctuation effect enhances the stability of a superconducting state, the theoretical approach starting from the standard Kohn-Sham scheme would be feasible.

In this study, we investigate charge fluctuation effects tractable in the multireference density functional theory (MR-DFT). The two-dimensional electronic structures of iron arsenides found in Kohn-Sham band structure calculations actually suggest a Cooper-pair hopping mechanism in layered materials. We derive an effective theory of superconductivity. Important point is weak interlayer single-electron hopping processes in iron arsenides. In our MR-DFT formalism, charge fluctuation modes are introduced by fixing the Kohn-Sham single-particle description as a mean-field limit of the theory. Here, a simple effective Bosonic Hamiltonian is derived for layered superconductors. The model tells us that the formation of the valence-bond-solid state in a bulk superconducting state enhances the stability of the ordered state via the appearance of hidden order parameters. A hypothesis on the stabilized superconducting state will be addressed, where minimized charge fluctuation leading to the $S = 1$ effective one-dimensional Heisenberg spin Hamiltonian is required for the most stable superconducting state in layered materials compared with other Heisenberg models with $S > 1$. This picture is confirmed if we assume that quasi-particles in the layered superconductor highly correlate. Discretized quasi-particle spectrum expected in correlated electron systems ensures the effective spin Hamiltonian.

To start discussion about the first-principles simulation method concrete, we address a new theory for the correlated electron systems called the density functional variational theory.
(DFVT). This is a simple variational method that always refers to a self-consistent solution given by MR-DFT. Finally, a means of applying the analysis techniques of DFVT to iron arsenide, as well as to other layered high-temperature superconductors including cuprates and MgB$_2$, will be addressed.

2. The Multireference Density Functional Theory

In the standard DFT, the explicit form of the charge fluctuation is given by the energy density functional:

$$E_{\text{fluc}}[n] = \frac{e^2}{2} \int_0^1 d\lambda \int d^3rd^3r' \frac{1}{|r-r'|} \langle \Psi^\lambda_n | (\hat{n}(r) - n(r))(\hat{n}(r') - n(r')) | \Psi^\lambda_n \rangle$$

$$- \frac{e^2}{2} \int_0^1 d\lambda \int d^3rd^3r' \frac{1}{|r-r'|} \langle \Psi^\lambda_n | \sum_\sigma \psi_\sigma^\dagger(r) \psi_\sigma(r') \delta(r - r') | \Psi^\lambda_n \rangle. \quad (1)$$

Here, $n(r)$ is the electron density, $\psi_\sigma(r)$ is the electron field operator for the spin $\sigma$, $\hat{n}(r) = \psi_\sigma^\dagger(r) \psi_\sigma(r)$, and $\Psi^\lambda_n$ is a minimizing wavefunction $\Psi'$ of the following reduced energy density functional

$$F_{\lambda}[n] = \min_{\Psi' \rightarrow n} \langle \Psi' | \hat{T} + \lambda \hat{V}_{ee} | \Psi' \rangle. \quad (2)$$

In the above definition, the kinetic energy operator $\hat{T}$ is

$$\hat{T} = -\frac{\hbar^2}{2m} \int d^3r \sum_{\sigma} \lim_{r' \rightarrow r} \psi_\sigma^\dagger(r') \Delta r \psi_\sigma(r), \quad (3)$$

where $m$ is the electron mass, and the Coulomb interaction is given in operator form as

$$\hat{V}_{ee} = \frac{1}{2} \int d^3rd^3r' \frac{e^2}{|r-r'|} \sum_{\sigma,\sigma'} \psi_\sigma^\dagger(r) \psi_\sigma^\dagger(r') \psi_{\sigma'}(r') \psi_{\sigma'}(r). \quad (4)$$

Although eq. (1) is an exact expression, it is not easy to obtain insight into relevant charge fluctuation modes in a solid only by considering the use of this functional form. This is partly because the form is written in double integrals with respect to electron positions $r$ and $r'$. However, we can see that the charge fluctuation may occur everywhere in the electron system. Once a crucial scattering due to the Coulomb fluctuation occurs between Fe$_2$As$_2$ layers, a pair scattering from one layer to another becomes a forward scattering.

In our multireference density functional theory, we can introduce part of the fluctuation explicitly by introducing a fluctuation term, $\langle \Psi | \hat{V}_{X_i} | \Psi \rangle$, with the self-interaction correction in the form

$$\langle \Psi | \hat{V}_{X_i} | \Psi \rangle = \sum_n X_i^{(n)} \langle \Psi | \left\{ \hat{Y}_i^{(n)} - \langle \hat{Y}_i^{(n)} \rangle \right\}^\dagger \left( \hat{Y}_i^{(n)} - \langle \hat{Y}_i^{(n)} \rangle \right) \right\} | \Psi \rangle$$

$$- \left\{ \hat{Z}_i^{(n)} - \langle \hat{Z}_i^{(n)} \rangle \right\}^\dagger \left( \hat{Z}_i^{(n)} - \langle \hat{Z}_i^{(n)} \rangle \right) \right\} | \Psi \rangle. \quad (5)$$

Since we may have a series of models, we use the notation $\langle \Psi | \hat{V}_{X_i} | \Psi \rangle$ with index $i$ specifying the number of the model. The notation $\hat{O}$ with an operator $\hat{O}$ denotes the normal ordering.
with respect to the creation and annihilation operators. The operators $\hat{Y}_i^{(n)}$ and $\hat{Z}_i^{(n)}$ may be given (i) by an expansion formula of the Coulomb operator around a fixed center and (ii) by a creation method for the Dirac character for the crystal. Definitions of each operators are given in the literature. Following the work,\textsuperscript{28} we introduce the notation $\Phi_{pLM}(r) = g_{pL}(r)Y_{LM}(\theta, \phi)$ and $\bar{\Phi}_{pLM}(r) = \bar{g}_{pL}(r)Y_{LM}(\theta, \phi)$ using the spherical harmonics $Y_{LM}$ and a complete set of $g_{pL}(r)$ expanding the radial waves. Another function $\bar{g}_{pL}(r)$ is

$$\bar{g}_{pL}(r) = \frac{1}{r^{L+1}} \int_0^r dr' (r')^L g_{pL}(r').$$

In our Coulomb operator expansion formula, the $Y$ and $Z$ operators are given by,

$$\hat{Y}_{pLM} = \frac{1}{\sqrt{2}} \int d^3r \sum_\sigma \psi^\dagger_\sigma(r) \left( \Phi_{pLM}(r) + \bar{\Phi}_{pLM}(r) \right) \psi_\sigma(r),$$

$$\hat{Z}_{pLM} = \frac{1}{\sqrt{2}} \int d^3r \sum_\sigma \psi^\dagger_\sigma(r) \left( \Phi_{pLM}(r) - \bar{\Phi}_{pLM}(r) \right) \psi_\sigma(r).$$

The $n$th operators $\hat{Y}_i^{(n)}$ and $\hat{Z}_i^{(n)}$ in the $i$th model may be given by identifying a parameter set $p, L, \text{ and } M$ as $n = (p, L, M)$. We have other possible expansions using a screened form of the Coulomb operator if we utilize DFVT given in the next section. The definitions of eqs. (7) and (8) are independent of the Kohn-Sham orbitals, which are used to expand the wavefunctions and the field operators in the creation and annihilation operators. This point gives an advantage to our formalism, because the scattering channels are defined before obtaining expressions of the Kohn-Sham orbitals.

We also use the notation $n_\Psi$ to represent a density associated with a state $|\Psi\rangle$ as $n_\Psi(r) \equiv \langle \Psi|\hat{n}(r)|\Psi\rangle$. The energy functional of the new extended Kohn-Sham scheme is

$$G_X[\Psi] = \langle \Psi|\hat{T} + \hat{V}_X|\Psi\rangle - \min_{\Psi' \rightarrow n_\Psi(r)} \langle \Psi'|\hat{T} + \hat{V}_X|\Psi'\rangle$$

$$+ \ F[n_\Psi] + \int d^3r v_{\text{ext}}(r)n_\Psi(r)$$

$$= \langle \Psi|\hat{T} + \hat{V}_X|\Psi\rangle + \frac{1}{2} \int \frac{n_\Psi(r)n_\Psi(r')}{|r - r'|}d^3rd^3r'$$

$$+ E_{\text{exc}}[n_\Psi] + \int d^3r v_{\text{ext}}(r)n_\Psi(r).$$

Here, we refer to the universal energy functional $F[n]$ given by

$$F[n] = \min_{\Psi' \rightarrow n} \langle \Psi'|\hat{T} + \hat{V}_{ee}|\Psi'\rangle.$$ \hspace{1cm} (10)

The definition of $E_{\text{exc}}[n]$ is given by eq. (9) itself. The new extended Kohn-Sham model is actually an effective many-body system.

When we let some of $X_i^{(n)}$ be finite, if we replace $E_{\text{exc}}[n]$ with the GGA energy functional $E_{\text{GGA}}[n_\Psi]$, the model becomes a correlated Fermion model, which is defined by the
approximated energy functional

\[ \hat{G}_{X_i}[\Psi] = \langle \Psi | \hat{T} + \hat{V}_{X_i} | \Psi \rangle + \frac{e^2}{2} \int d^3r d^3r' \frac{n_\Psi(r)n_\Psi(r')}{|r-r'|} + E_{GGA}[n_\Psi] + \int d^3r v_{ext}(r)n_\Psi(r). \]  

(11)

The two-body scattering process happening in the \( i \)-th model is derived from the fluctuation term, which is divided into the effective two-body interaction and a counter term as

\[ \frac{\delta \langle \Psi | \hat{V}_{X_i} | \Psi \rangle}{\delta \langle \Psi \rangle} = \mathcal{H}_i^2 + \mathcal{H}_{i,\text{counter}}^1. \]  

(12)

\[ \mathcal{H}_i^2 = \sum_n X_i^{(n)} \left\{ \left( \hat{Y}_i^{(n)} \right)^\dagger \hat{Y}_i^{(n)} + \left( \hat{Z}_i^{(n)} \right)^\dagger \hat{Z}_i^{(n)} \right\}, \]  

(13)

\[ \mathcal{H}_{i,\text{counter}}^1 = -\sum_n X_i^{(n)} \left\{ \left( \hat{Y}_i^{(n)} \right)^\dagger \hat{Y}_i^{(n)} + \left( \hat{Z}_i^{(n)} \right)^\dagger \hat{Z}_i^{(n)} \right\} - (\hat{Z}_i^{(n)})^\dagger \hat{Z}_i^{(n)} - (\hat{Z}_i^{(n)})^\dagger \hat{Z}_i^{(n)} \} \].  

(14)

Since we have the exchange-correlation potential for GGA as

\[ \mu_{GGA}(r) = \frac{\delta E_{GGA}[n]}{\delta n(r)}, \]  

(15)

a secular equation is derived by imposing the normalization condition of \( |\Psi\rangle \) using the Lagrange multiplier \( E \) as,

\[ \frac{\delta \hat{G}_{X_i}[\Psi]}{\delta \langle \Psi \rangle} = \mathcal{H}_i^{\text{eff}} |\Psi\rangle = E |\Psi\rangle, \]  

(16)

\[ \mathcal{H}_i^{\text{eff}} = \mathcal{H}_i^1 + \mathcal{H}_i^2 + \mathcal{H}_{i,\text{counter}}^1, \]  

(17)

\[ \mathcal{H}_i^1 = \hat{T} + \int \hat{v}_{\text{eff}}(r)\hat{n}(r)d^3r. \]  

(18)

The effective single particle potential \( \tilde{v}_{\text{eff}}(r) \) is given by

\[ \tilde{v}_{\text{eff}}(r) = \int \frac{n(r')}{|r-r'|}d^3r' + \mu_{GGA}(r) + v_{\text{ext}}(r). \]  

(19)

We have a potential problem given as,

\[ \left\{ \frac{\hbar^2}{2m} \Delta r + \tilde{v}_{\text{eff}}(r) \right\} \chi_{m,k,k_z}(r) = \varepsilon_{m,k,k_z} \chi_{m,k,k_z}(r), \]  

(20)

in which Bloch orbitals \( \chi_{m,k,k_z}(r) \) are determined to be normalized and orthonormal in a crystal phase. Here, the Kohn-Sham orbital is specified by a two-dimensional wave vector, \( k \), another wave vector, \( k_z \), along the \( c \) axis, and the band index \( m \).

We do not explicitly write the \( i \) dependence on \( \mathcal{H}_i^1 \). However, it is implicitly dependent on the fluctuation term \( \langle \Psi | \hat{V}_{X_i} | \Psi \rangle \) through the self-consistency on the charge density \( n(r) = n_\Psi(r) \). We may have another definition of a single-particle problem by including the nonlocal potential part and/or mean-field part coming from \( \langle \hat{Y}_i^{(n)} \rangle \) and \( \langle \hat{Z}_i^{(n)} \rangle \), i.e. the 1-body counterterm \( \mathcal{H}_{i,\text{counter}}^1 \). However, this shift only changes the definition of single-particle or-
Itals used to determine the many-body problem. The charge density \( n_\Psi(r) \) determines the expectation values \( \langle \hat{Y}_i^{(n)} \rangle \) and \( \langle \hat{Z}_i^{(n)} \rangle \). Thus, if \( n_\Psi(r) \) is almost unchanged in a self-consistent loop, these values also remain unchanged. Even if there are many-body correlation effects creating a few meV of gap in the model, the essential features of the GGA band structure are unaffected by only the part \( \mathcal{H}_i^{\text{counter}} \). An essential change may occur via the correlation effects appearing as a slight change in \( n_\Psi(r) \) and a large change in variational energy via \( \mathcal{H}_i^2 \).

When \( X_i^{(n)} = 0 \) for all \( n \) values, we obtain a secular equation of the Kohn-Sham equation in GGA given by eq. (20). The ground state of this model is slightly shifted from the final state, when we consider a correlated electron system. The obtained single-particle description defines the Kohn-Sham band structure. Introducing a proper Fourier transformation for a selected set of bands, we immediately obtain the Wannier representation, allowing us to rewrite \( \mathcal{H}_i^{\text{eff}} \) in a second-quantized form of a tight-binding model.

In the GGA calculation, we may consider the spin density by introducing a spin-dependent GGA functional. If we adopt the spin-GGA scheme, the Kohn-Sham equation becomes spin-dependent for a magnetic solution. For the formulation of MR-DFT, however, spin-independent Kohn-Sham orbitals are very useful for the discussion of magnetism and superconductivity. This is because the correlation effects are described by the multireference variational states, i.e. the multi-Slater determinants, in MR-DFT. Thus our starting point is a paramagnetic state obtained by a nonmagnetic GGA calculation.

3. Pair-Hopping Mechanism

In the first-principles study of compound superconductors, we may apply the Kohn-Sham scheme\(^{24} \) of the density functional theory (DFT)\(^{29} \) as a starting point. Thus, we investigate Kohn-Sham band structures, which are known in the literature or found in actual calculation results. The important points considered here are the structures of the Fermi surface and the dimensionality of the low-energy branches of the band structure.

The pictures drawn from the study summarized in the last section are as follows. We have several examples of iron arsenides, which have two-dimensional Fermi surfaces, within the Kohn-Sham scheme. Details of the Fermi surfaces actually depend on the type of material. However, in general, the GGA band structure suggests a picture of a stack of \( \text{Fe}_2\text{As}_2 \) layers weakly coupled by single-particle tunneling at the Fermi level.

If we expect Fermi instability due to the remaining Coulomb fluctuation modes lost in a mean-field approach, or if relevant fluctuation only shifts the electronic structure around the Fermi level by opening a gap of a few tens meV, only a slight change in the total charge density due to appearance of secondary order parameters is expected. Then, a picture of the layered two-dimensional Fermi gas system should remain as a starting one-body mean-field state even in the final many-body solution affected by correlation effects.

In this picture, we need to incorporate effective two-body interactions both within a layer
and between layers. Here, note that there is no interband single-particle hopping process, since the single-particle part is diagonal in the band index. A step to maintain self-consistency is necessary after solving the many-body problem given by the effective two-body repulsive interactions, since the charge redistribution might or might not modify the effective single-particle excitation spectrum at approximately the Fermi level.

The stacking of two-dimensional systems in one direction forms a layered bulk system. The system becomes a correlated electron system, because the single-electron tunneling process is reduced owing to the two-dimensionality and because possible charge fluctuations in a layer should be suppressed also owing to the localized nature of Fe 3d orbitals in the superconductor. This picture is tractable by constructing a one-dimensional Wannier representation from the Kohn-Sham orbitals. The band dispersions around the Fermi level are almost flat along the c-direction, so that the one-dimensional Wannier representation is natural.

The motion of electrons in a layer is described by a two-dimensional electron gas model. Here, a two-dimensional wave vector $\mathbf{k}$ and a band index $m$, or a combined index $j = (m, k)$, are used to specify each Wannier state in the $l$-th layer. In the two-dimensional system with multicolored Fermion quasi-particles in the layer, a reduced model might be well-described by a known two-dimensional model.\(^{22,30}\) In such a model, the effective electron-electron interaction parameters would specify intralayer scattering processes. A superconducting fluctuation may occur, if we consider the two-body scattering processes due to charge or spin fluctuations, which is not explicitly counted in the GGA calculation. The electron-phonon interaction may contribute to the stability of the superconducting fluctuation in the layer. For our next discussion, however, intralayer effective attractions can originate from any mechanism, as far as it effectively supports the formation of the precursors of the bulk superconducting order parameter.

Here, the important driving force derived in this study is the interlayer pair-hopping processes between the layers. When the Kohn-Sham orbitals are determined using the effective exchange-correlation potential, $v_{xc}(\mathbf{r})$, these charge fluctuation modes are not included explicitly. In MR-DFT, the modes are explicitly introduced using two-body operators. The two-body processes are given by the repulsive nature of the Coulomb electron-electron scattering. If we have any effective attractive interaction at a position between the layers, the mechanism is lost. The origin of the charge fluctuation effect will now be discussed in detail.

We consider the Wannier representation of orbitals localized in a layer. The orbital wavefunction has a representation $\phi_{jl}(\mathbf{r})$ without an explicit spin dependence. Actually, we can use a proper unitary transformation, e.g., the Wannier transformation, to create $\phi_{jl}(\mathbf{r})$ from $\chi_{m,k,k_z}(\mathbf{r})$. Here, $l$ denotes an index of a layer and $j$ represents a set of indexes $(m, k)$. By associating creation and annihilation operators, $c_{jl}^\dagger$ and $c_{jl}$ are defined by the Canonical anti-
commutation relation,
\[ \{ c_{j\sigma}^\dagger, c_{j'\sigma'} \} = \delta_{jj'} \delta_{\sigma\sigma'}. \]  

(21)

As a relevant perturbation for the GGA band structure, we consider scattering processes coming from the charge fluctuation in \( \langle \Psi|\hat{V}_X|\Psi \rangle \). In the expression of the \( Y \) and \( Z \) operators, we have a pair of field operators, namely, \( \psi_{\sigma}^\dagger (r) \) and \( \psi_{\sigma} (r) \). These operators are expanded in the localized orbitals \( \phi_{j\sigma}(r) \) and \( c_{j\sigma}^\dagger, c_{j\sigma} \). Thus, we notice that we have a double summation in the definitions of \( \hat{Y}_{i}^{(n)} \) and \( \hat{Z}_{i}^{(n)} \). One is for the conserved quantities and the other is with respect to the orbitals in the Wannier form. Here, the center for the Coulomb expansion formula is not necessarily identical to a Wannier center. Depending on the symmetry of an electron pair in both the initial and final states, the proper selection of \( n = (p, L, M) \) is given to minimize the energy using DFVT. We can then identify relevant fluctuation terms, in which \( \hat{Y}_{i}^{(n)} \) may connect a localized orbital in the low-energy bands at the Fermi energy with other semilocalized orbitals, leading to the pair hopping between Wannier centers.

When a superconducting order parameter \( \bar{\Delta}(r, r') \equiv \sum_{(j j')} \phi_{j\sigma}(r) \phi_{j'\sigma'}(r') \langle c_{j\sigma} c_{j'\sigma'} \rangle \) is expected to be finite, each term in \( \langle \Psi|\hat{V}_X|\Psi \rangle \) can be re-expressed as below. As an example, we consider the expression

\[
X_{i}^{(n)}(\Psi) : \left( \hat{Y}_{i}^{(n)} - \langle \hat{Y}_{i}^{(n)} \rangle \right) \left( \hat{Y}_{i}^{(n)} - \langle \hat{Y}_{i}^{(n)} \rangle \right) : | \Psi \rangle
= X_{i}^{(n)} \left\{ \langle \Psi | : \left( \hat{Y}_{i}^{(n)} \right) \left( \hat{Y}_{i}^{(n)} \right) : | \Psi \rangle - \left( \left( \hat{Y}_{i}^{(n)} \right) \right) \langle \hat{Y}_{i}^{(n)} \rangle \right\}
= \sum_{l_{1}l_{2}l_{3}l_{4}l'_{1}l'_{2}j_{1}j_{2}j_{3}j_{4}} \sum_{\sigma, \sigma'} \frac{X_{i}}{2} \int d^{3}r \int d^{3}r' \phi_{j_{1}l_{1}}^{\ast}(r) \left( \Phi_{pLM}(r) + \bar{\Phi}_{pLM}(r) \right) \phi_{j_{4}l_{4}}(r) \times \phi_{j_{2}l_{2}}(r) \left( \Phi_{pLM}(r) + \bar{\Phi}_{pLM}(r) \right) \phi_{j_{3}l_{3}}(r) ; c_{j_{1}l_{1}\sigma}^\dagger c_{j_{4}l_{4}\sigma} c_{j_{2}l_{2}\sigma'} c_{j_{3}l_{3}\sigma'} : - X_{i}^{(n)} \left( \left( \hat{Y}_{i}^{(n)} \right) \right) \langle \hat{Y}_{i}^{(n)} \rangle
= \sum_{l_{1}=l_{2}=l_{3}=l_{4}=l'_{1}=l'_{2}=j_{1}=j_{2}=j_{3}=j_{4}} \sum_{\sigma, \sigma'} g_{n;llll;j_{1}j_{2}j_{3}j_{4}} \left\{ \left( c_{j_{1}l_{1}\sigma}^\dagger c_{j_{4}l_{4}\sigma} c_{j_{2}l_{2}\sigma'} c_{j_{3}l_{3}\sigma'} : \right) - X_{i}^{(n)} \left( \left( \hat{Y}_{i}^{(n)} \right) \right) \langle \hat{Y}_{i}^{(n)} \rangle \right\}
\]

(22)

Here, the coefficient \( g_{n;llll;j_{1}j_{2}j_{3}j_{4}} \) is given by

\[
g_{n;llll;j_{1}j_{2}j_{3}j_{4}} = \frac{X_{i}^{(n)}}{2} \int d^{3}r \int d^{3}r' \phi_{j_{1}l_{1}}^{\ast}(r) \left( \Phi_{pLM}(r) + \bar{\Phi}_{pLM}(r) \right) \phi_{j_{4}l_{4}}(r) \times \phi_{j_{2}l_{2}}^{\ast}(r') \left( \Phi_{pLM}(r') + \bar{\Phi}_{pLM}(r') \right) \phi_{j_{3}l_{3}}(r').
\]

(23)
A similar expansion is also given for terms with the $\hat{Z}_i^{(n)}$ operators. Thus, the effective two-body Hamiltonian $H_i^2$ is divided into three parts: (1) the intralayer two-body Hamiltonian $H_{i,\text{intra}}^2$ (with $g_{n;llll,j1j2j3j4}$), (2) the interlayer pair hopping Hamiltonian $H_{i,\text{inter}-\text{pair}}^2$ (with $g_{n;lll'l',j1j2j3j4}$), and (3) other 2-body terms $H_{i,\text{inter}-\text{res}}^2$.

The first category $H_{i,\text{intra}}^2$ contains terms interpreted as the on-site Hubbard repulsion. However, to obtain an explicit form, we need to introduce another Wannier transformation to have Wannier orbitals localized around a Wannier center in a layer. This process might be difficult, since we need to introduce unitary transformation in a rather wide energy window over a few eV. In our discussion, this process is not required to derive an effective low-energy model of high-temperature superconductors. In $H_{i,\text{intra}}^2$, we also have intralayer exchange interaction, intralayer off-site repulsion, and intralayer pair hopping. These effective interactions may induce the spin fluctuation effect as well as the charge fluctuation effect. For a general discussion, we do not specify the detailed form of $H_{i,\text{intra}}^2$, thereby allowing a BCS model Hamiltonian for the electron-phonon mechanism, a correlated two-dimensional electron model, and a model considering both effects. In our pair-hopping mechanism, $H_{i,\text{inter}-\text{pair}}^2$ plays a relevant role.

Note that $X^{(n)}_i$ is finite for a selected set of $p$, $L$, and $M$ values. The second category $H_{i,\text{inter}-\text{pair}}^2$ is derived from a representation as a mean-field term plus the fluctuation term using the superconducting order as in eq. (22). The third category $H_{i,\text{inter}-\text{res}}^2$ contains interlayer exchange interaction, inter-layer correlated hopping terms and interlayer diagonal charge fluctuation. We express the interlayer two-body Hamiltonian as $H_{i,\text{inter}}^2 = H_{i,\text{inter}-\text{pair}}^2 + H_{i,\text{inter}-\text{res}}^2$.

The effective model may be written in a second quantized form as

$$H_{\text{eff}} = H_{\text{intra}}^1 + H_{i,\text{intra}}^2 + H_{i,\text{inter}}^1 + H_{i,\text{inter}}^2 + H_{i,\text{counter}},$$

$$H_{\text{intra}}^1 = \sum_l \sum_{\langle jj' \rangle} \sum_\sigma c_{lj\sigma}^\dagger c_{lj' \sigma} \{ c_{lj\sigma}^\dagger c_{lj' \sigma} + \text{H.c.} \},$$

$$H_{\text{inter}}^1 = \sum_{l \neq l'} \sum_{\langle jj' \rangle} \sum_\sigma c_{lj\sigma}^{(ll')} \{ c_{lj\sigma}^\dagger c_{lj' \sigma} + \text{H.c.} \},$$

where $H_{\text{intra}}^1$ is the intralayer single-body Hamiltonian and $H_{\text{inter}}^1$ is the interlayer single-body Hamiltonian. The index $l$ specifies an $l$-th layer and $j$ represents a $j$-th orbital in the $l$-th layer. Note again that the $j$-th orbital is a Wannier representation made by one-dimensional Fourier transformation from the Bloch waves. Thus, we can always say that the interlayer single-body process for the Wannier states around the Fermi level is negligible for iron-arsenide superconductors. At energy levels above the Fermi level, however, we also have finite bandwidths for the GGA band structure in the $c$ direction. This picture is very important for the discussion below.

We now construct a standard model of high-temperature superconductivity. Two steps are necessary. First is the construction of a mean-field description and second is the derivation...
of the many-body effective Hamiltonian. We consider the effective intralayer Hamiltonians $\mathcal{H}^{1}_{\text{intra}}$ and $\mathcal{H}^{2}_{\text{intra}}$, which induce superconducting fluctuation. However, owing to their explicit two-dimensionality, $\mathcal{H}^{1}_{\text{intra}} + \mathcal{H}^{2}_{\text{intra}}$ cannot induce bulk superconductivity by itself. We then introduce the mean-field description of a two-dimensional superconducting state on a layer in a self-consistent field of other layers. Here, let us consider singlet superconductivity. The order parameter $\Delta_l(r, r') \equiv \sum_{jj'} \phi_{jl}(r)\phi_{jl}(r')\langle c_{jl}c_{jl}' \rangle$ can have a finite value around the $l$-th layer. One important point is that $\Delta_l(r, r')$ may change its phase as $(-1)^l$, but the following theory also allows a constant phase factor for all layers. The final superconducting phase should be determined by a variational determination method.

We may consider two-body fluctuation, which induces pair-hopping processes between neighboring layers. The process comes from $\mathcal{H}^{2}_{\text{inter-pair}}$. This term results in a pair field Hamiltonian for the $l$-th layer.

$$\mathcal{H}^{\text{pf}}_l = \sum_n X_i^{(n)} \int d^3r d^3r' \sum_{l' \neq l} \sum_{jj'} \{ \Delta^*_{l'}(r, r') \left( \Phi_{pLM}(r)^* \times \Phi_{pLM}(r') + H.c. \right) \\
+ \Phi_{pLM}(r)^* \times \Phi_{pLM}(r') \phi_{jl}(r)\phi_{jl}(r')c_{jl}c_{jl}' + H.c. \}.$$  

We have introduced an effective coupling constant $X_i^{(n)}$ for each scattering channel described by $\left( \hat{Y}_i^{\text{(n)}} \right)^\dagger \hat{Y}_i^{\text{(n)}} - \left( \hat{Z}_i^{\text{(n)}} \right)^\dagger \hat{Z}_i^{\text{(n)}}$. It can be derived from the Coulomb kernel $\frac{e^2}{2|\mathbf{r} - \mathbf{r}'|}$, however, in the multireference density functional theory, effective coupling can be optimized. By applying the fluctuation reference method, we should determine the parameter for reproducing another precise calculation. Or the effective Hamiltonian can be determined using DFVT, which will be addressed in the next section. A relevant point in our discussion is that the model is derived using the multireference density functional theory.

The above derivation of eq. (27) is given by direct pair hopping. This Coulomb off-diagonal element is negligible for LaFeAsO$_{1-x}$F$_x$, since the neighboring two iron layers are widely separated by a La$_2$(O$_{1-x}$F$_x$)$_2$ layer. However, we have a pair-tunneling process across the insulating layer. We call it the super pair tunneling. To be precise, we show the construction step of the effective Hamiltonian for doped LaFeAsO. We can perform the non-magnetic GGA calculation of, e.g., LaFeAsO$_{0.875}$F$_{0.125}$ using a super cell with an optimized atomic position. The GGA band structure reveals the appearance of well-localized 3d bands of iron at the Fermi level. Both electron and hole pockets are created from the localized 3d orbitals. These center bands have a clear two-dimensionality. Above these bands, at approximately $3 \sim 4$ eV higher than the Fermi level, we have delocalized bands that consist of non-s orbitals at La sites and void sites between a Fe$_2$As$_2$ layer and a La$_2$O$_2$ layer. These extended bands are formed by the hybridization between these high energy levels and iron 3d orbitals, so that localized 3d orbitals connect to higher levels using finite matrix elements by two-body Coulomb scattering.
processes. With the help of these orbitals, an indirect pair-hopping process from a Fe$_2$As$_2$ layer to the next layer by Coulomb off-diagonal elements is allowed. This second-order perturbation process is relevant. Its effective form finally becomes the same as $\mathcal{H}^2_{i,\text{inter-pair}}$, if we replace the interaction kernel with the effective one. We could also have a higher-order contribution from other terms in $\mathcal{H}^2_{i,\text{inter-res}}$ for the pair-field Hamiltonian. However, it is important to note that $\mathcal{H}^1_{\text{inter}}$ is always necessary to have the energy reduction in the superconducting state, since $\mathcal{H}^1_{\text{intra}}$ is negligible at the Fermi energy and since $\mathcal{H}^1_{\text{inter}}$ is diagonal in the band index.

For 11 compounds, we may consider only orbitals in a Fe$_2$Se$_2$ layer or a Fe$_2$Te$_2$ layer. In these systems, a direct pair hopping from one layer to the next layer is possible via Coulomb repulsion. Thus, we have two different categories of the pair-hopping mechanism. The first is the direct pair hopping and the second is the indirect super pair tunneling. Both of the processes require a finite amplitude for the pair hopping from a localized orbital to another well-defined orbital.

The inclusion of the pair field necessarily results in a Josephson coupled superconducting state as a variational ground state. Its local wavefunction is given by the following effective Hamiltonian for the $l$-th layer:

$$\mathcal{H}^l_{\text{eff}} = \sum_{\langle jj'\rangle} \sum_{\sigma} t^{(l)}_{jj'} \left\{ c_{j\sigma}^\dagger c_{j'\sigma}^\dagger + \text{H.c.} \right\} + \mathcal{H}^2_{i,\text{intra},l} + \mathcal{H}^l_{\text{pf}}, \quad (28)$$

where the intralayer two-body Hamiltonian $\mathcal{H}^2_{i,\text{intra},l}$ for the $l$-th layer can be either electron-electron-interaction originated, electron-phonon-interaction originated, or their combination. The pair-hopping processes producing $\mathcal{H}^l_{\text{pf}}$ can give energy gain to the Coulombic electron system, although a finite energy loss occurs when single-particle tunneling processes between layers induced by $\mathcal{H}^l_{\text{inter}}$ are terminated to have a variational state, even if they are negligible.

In the mean-field description, we are able to obtain a mean-field solution, which have two order parameters: $n(r)$ and $\bar{\Delta}_l(r, r')$. In the MR-DFT formalism, appearance of $\bar{\Delta}_l(r, r')$ affects the single-particle momentum distribution and its Fourier transform, i.e. $n(r)$. Therefore, we can interpret that $n(r)$ becomes $\bar{\Delta}_l$-dependent. For the derivation, however, we need techniques for discretizing several continuous variables to have a tractable model in MR-DFT simulation. Here, we would rather move onto another effective theory to consider the superconducting phase derived from interlayer pair-hopping processes.

When a mean-field wavefunction of the layered material is obtained in the form

$$|\Psi^{(0)}\rangle = \prod_l \prod_{mk} \otimes \left( u^{(l)}_{mk} + v^{(l)}_{mk} b^\dagger_{mk} \right) |0\rangle, \quad (29)$$

we can consider an explicit pair hopping. Here, $b^\dagger_{mk} = c^\dagger_{mk\ell} c^\dagger_{m-\ell k\ell}$ with $c^\dagger_{mk\sigma} = c^\dagger_{j\ell\sigma}$, where $m$ is the band index and $k$ is the two-dimensional wave vector. The real factor $u^{(l)}_{mk}$ and another complex factor, $v^{(l)}_{mk}$, satisfy $\left( u^{(l)}_{mk} \right)^2 + \left( v^{(l)}_{mk} \right)^2 = 1$. However, note that, even if we have a correlated superconducting state $|\Psi^{(0)}\rangle$ with an expression other than eq. (29), we can always
construct a Bogoliubov-Valatin transformation using the superconducting order parameter $\Delta(r, r')$.

Now we go to the final step in order to take the fluctuation effect into account and to obtain the hidden order parameter and the energy gap. When a pair described by $b_{mk}^{\dagger}$ hops via the annihilation operation $\Delta_{l}(r, r') \equiv \sum_{(j,j')} \phi_{jl}(r) \phi_{j'l}(r') c_{j+l} c_{j'+l}$, the layer loses two electrons and the next layer obtains these electrons (see Fig. 1(a)). Each layer should keep its charge neutrality, except for local charge fluctuation. Thus, if charge fluctuation effects are introduced into $|\Psi^{(0)}\rangle$, an effective action appears for this motion of pairs in the array of layers. (Fig. 1(b).) Then, we obtain a perturbed state $|\Psi^{(1)}\rangle$, which is determined by the effective action of the pairs. We derive the effective action using only a unitary transformation without referring to these supposed state vectors.

The charging effect should be of the same order of magnitude as the pair-hopping process. If the intralayer coherence is well kept, but if the interlayer single-electron hopping processes are not relevant, the screening effect expected for the system mainly occurs in the layer. The condition for $H_{\text{inter}}^{1}$ is consistent with this picture. Then, the number of pairs allowed to hop at one time in a fluctuation process is restricted to be very small.

To justify this discussion, we introduce the Josephson-Bardeen modification\textsuperscript{32,33} of the Bogoliubov-Valatin transformation:

\[
\begin{align*}
\hat{\gamma}_{emk|l}^{\dagger} &= u_{mk}^{(l)} c_{mkl}^{\dagger} - v_{mk}^{(l)} S_{l}^{*} c_{m-k|l}, \\
\hat{\gamma}_{hmk|l}^{\dagger} &= u_{mk}^{(l)} S_{m-k|l}^{*} - v_{mk}^{(l)} S_{l}^{*} = S_{l}^{*} \hat{\gamma}_{emk|l}, \\
\hat{\gamma}_{emk|l}^{\dagger} &= u_{mk}^{(l)} c_{m-k|l}^{\dagger} + \left(S_{l}^{*}\right)^{k} S_{m-k|l}, \\
\hat{\gamma}_{hmk|l}^{\dagger} &= u_{mk}^{(l)} S_{m-k|l}^{*} + \left(S_{l}^{*}\right)^{k} c_{m-k|l} = S_{l}^{*} \hat{\gamma}_{emk|l},
\end{align*}
\]

where $S_{l}$ annihilates a coherent pair in the condensate of the $l$-th layer and $S_{l}^{*}$ creates one. It is not necessary to have the form of $b_{mk}^{\dagger}$. Inserting the inverse transformation to a pair-hopping process, we find that

\[
\begin{align*}
c_{mk+p|l} c_{m-k-p|l}^{\dagger} c_{m'|k'|l}^{\dagger} c_{m'-k'|l} &= \left(u_{mk+p}^{(l)} \hat{\gamma}_{emk|l}^{\dagger} + v_{mk+p}^{(l)} S_{l}^{*}\hat{\gamma}_{emk|l}^{\dagger} \right) \left(u_{mk+p}^{(l)} \hat{\gamma}_{emk|l}^{\dagger} - v_{mk+p}^{(l)} S_{l}^{*}\hat{\gamma}_{emk|l}^{\dagger} \right) \\
&\times \left(u_{m'k}^{(l')} \hat{\gamma}_{emk'|l'}^{\dagger} + v_{m'k}^{(l')} S_{l'}^{*}\hat{\gamma}_{emk'|l'}^{\dagger} \right) \left(u_{m'k}^{(l')} \hat{\gamma}_{emk'|l'}^{\dagger} - v_{m'k}^{(l')} S_{l'}^{*}\hat{\gamma}_{emk'|l'}^{\dagger} \right) \\
&= \left(u_{mk+p}^{(l)} \hat{\gamma}_{emk|l}^{\dagger} + v_{mk+p}^{(l)} S_{l}^{*}\hat{\gamma}_{emk|l}^{\dagger} \right) \left(u_{mk+p}^{(l)} \hat{\gamma}_{emk|l}^{\dagger} - v_{mk+p}^{(l)} S_{l}^{*}\hat{\gamma}_{emk|l}^{\dagger} \right) \\
&\times \left(u_{m'k}^{(l')} \hat{\gamma}_{emk'|l'}^{\dagger} + v_{m'k}^{(l')} S_{l'}^{*}\hat{\gamma}_{emk'|l'}^{\dagger} \right) \left(u_{m'k}^{(l')} \hat{\gamma}_{emk'|l'}^{\dagger} - v_{m'k}^{(l')} S_{l'}^{*}\hat{\gamma}_{emk'|l'}^{\dagger} \right) \\
&- u_{mk+p}^{(l)} v_{mk+p}^{(l)} S_{l}^{*} \hat{\gamma}_{emk|l}^{\dagger} \hat{\gamma}_{emk|l} + u_{m'k}^{(l')} v_{m'k}^{(l')} S_{l'}^{*} \hat{\gamma}_{emk'|l'}^{\dagger} \hat{\gamma}_{emk'|l'} - u_{m'k}^{(l')} v_{m'k}^{(l')} S_{l'}^{*} \hat{\gamma}_{emk'|l'}^{\dagger} \hat{\gamma}_{emk'|l'}
\end{align*}
\]
For simplicity, we omit the radial dependences of $u_{l'}^{\ell'}$ and $v_{l'}^{\ell'}$. We can do a rough estimation of the relative distance between two quasi-electrons in real space.

To determine the localized nature of the hopping pair, we can do a rough estimation of the relative distance between two quasi-electrons in real space. For simplicity, we omit the radial dependences of $u_{m'k}^{\ell'}$ and $v_{m'k}^{\ell'}$, keeping only the energy dependences. Since we perform integrations in the $k$ space, by considering a superconducting gap much smaller than the Kohn-Sham-band width of a few eV, we have the following simplified expression for the creation operator of a hopping pair in an $m$-th band at an $l$-th layer from the next $l'$-th layer:

$$
\int d^2kd\varepsilon \sum_{m'k} (u_{m'k+p}^{\ell'})^2 u_{m'k}^{\ell'} v_{m'k}^{\ell'} \hat{c}_{m'k+p}^{\ell'} \hat{c}_{m'k}^{\ell'} S_{l'}^{\ell'}.
$$

(30)

Thus, we have a tunneling process from a Cooper pair in a condensate in a layer to a pair of quasi-electrons in the next layer by the contribution $(u_{m'k+p}^{\ell'})^2 u_{m'k}^{\ell'} v_{m'k}^{\ell'} \hat{c}_{m'k+p}^{\ell'} \hat{c}_{m'k}^{\ell'} S_{l'}^{\ell'} + \text{H.c.}$, which is found in the above expression.

In a correlated quasi-electron system of the $l$-th superconducting layer, the charge fluctuation mode in $\mathcal{H}_{\text{intra}}^{\ell}$ produces short-range repulsive terms for the quasi-electron state given by $\hat{c}_{l'mkl}^{\ell'}$ and $\hat{c}_{l'kmkl}^{\ell'}$. Since pair hopping occurs at a local position, the quasi-electrons in a pair inevitably raise their energy. To determine the localized nature of the hopping pair, we can do a rough estimation of the relative distance between two quasi-electrons in real space. For simplicity, we omit the radial dependences of $u_{m'k}^{\ell'}$ and $v_{m'k}^{\ell'}$, keeping only the energy dependences. Since we perform integrations in the $k$ space, by considering a superconducting gap much smaller than the Kohn-Sham-band width of a few eV, we have the following simplified expression for the creation operator of a hopping pair in an $m$-th band at an $l$-th layer from the next $l'$-th layer:

$$
\int d^2kd\varepsilon \sum_{m'k} (u_{m'k+p}^{\ell'})^2 u_{m'k}^{\ell'} v_{m'k}^{\ell'} \hat{c}_{m'k+p}^{\ell'} \hat{c}_{m'k}^{\ell'} S_{l'}^{\ell'}.
$$

(31)

Here, $E_F$ is the Fermi energy of the Kohn-Sham band structure and we have omitted the $k_z$ dependence of Kohn-Sham energy owing to its two-dimensional nature. If we further consider a semimetallic band with the $m$-th conduction band, the above expression indicates that a contribution of doubly occupied Wannier states appears. In iron arsenide, this Wannier state should be in a localized 3$d$ state at an iron site.

The above-mentioned characteristic feature of the Hubbard-type correlated system is very important in considering layered superconductors with 3$d$ local orbitals. The pair-hopping process from the condensate to a correlated quasi-particle state leads to the conclusion of a discretized energy spectrum as a function of the number of hopping processes at a time. In other words, depending on the number of quasi-particle pairs, $n_{\text{pair}}$, and $m_{\text{pair}}$ of pair holes in a layer, we obtain the energy contribution of $E(n_{\text{pair}}, m_{\text{pair}}) = U_e n_{\text{pair}} + U_h m_{\text{pair}}$ with the effective parameters $U_e > 0$ and $U_h > 0$. A simple correspondence of $n_{\text{pair}}$ in the physics of the Hubbard model is shown by the number of doubly occupied sites.

Let's therefore consider the situation given in Fig. 1(b), where only one pair is left from one layer to another layer. The bosonic nature of the pair allows us to write down an effective Hamiltonian in a Heisenberg spin system. Since we have a hopping pair or a vacancy at a layer, we have at least three states for each layer. We can assign these states to $S_z = \pm 1$ and
$S_z = 0$ of an artificial spin state and introduce an effective spin Hamiltonian. This minimal case is an $S = 1$ system, in which the $l$-th layer may have one of these three states: $S_z = 0$ and $\pm 1$.

Now, the pair-hopping process is described by the $xy$-term in the Heisenberg model. Neighboring charges with different signs will lower the energy, but two neighboring pairs with the same sign will raise the energy. This contribution is described by the anti-ferromagnetic $z$-term in the Heisenberg exchange interaction. The charge neutrality discussed above also leads on-site anisotropy, i.e. the $D$ term, to stabilize the $S_z = 0$ state, which corresponds to a neutral layer. These contributions are described by an XXZ model with the $D$ term. If a semimetallic band structure is the starting limit, and if the charge imbalance is minimized, the effective local charge neutrality is expressed by local energy enhancement, which is symmetric with quasi-particle pairs and pair holes, then a simple $D$ term should appear. In general, the charge neutrality condition can be effectively expressed by the introduction of a $D$ term. Thus, the minimal model is a one-dimensional anisotropic $S = 1$ Heisenberg antiferromagnetic spin chain.

$$\mathcal{H}_{\text{AFHM}} = \sum_l \left[ J (S^x_l S^x_{l+1} + S^y_l S^y_{l+1}) + J_z S^z_l S^z_{l+1} \right] + D \sum_l (S^z_l)^2. \quad (32)$$

We know that there are three gapped phases in this model: the Néel phase, large-D phase, and Haldane phase. The Néel phase corresponds to a pair-vacancy array in the present model. The state thus corresponds to a charge density wave state along the stacking direction. Thus, it is not relevant for the present consideration for the superconductor. The large-D phase corresponds to a Mott insulating phase, where the charge fluctuation effect is suppressed. In the limiting case in the large-D phase, a decoupled array of two-dimensional electron gas is realized owing to the suppression of the charge fluctuation. For a relevant contribution to stabilize a bulk superconductor, the Haldane phase is the necessary phase. In the Haldane phase, a valence-bond-solid state is realized with a broken hidden string order parameter. This gapped state with a hidden extra order contributes to the stabilization of bulk superconductivity. The phase diagram of the antiferromagnetic $S = 1$ XXZ chain with uniaxial single-ion anisotropy is extensively studied.

The Haldane phase possesses an excitation gap. The lowest excitation with a total effective spin $S^z_{\text{tot}} = 1$ corresponds to the creation of an extra Cooper pair in the bulk. In this state, the number of bosons actually increases by one. When the effective model has $J = J_z = 1$ with $D = 0$, the gap becomes $\Delta \simeq 0.410479 J$. There are continuous series of trials for determining Haldane gap. Recently, Ueda et al. have provided an estimation of lower and upper bounds and concluded that the gap is in $[0.41047905, 0.41047931]$. This study is performed by the combined use of the hyperbolic-deformation technique and sequence interval squeeze method. When interaction parameters are varied, the gap changes continuously in the Haldane phase.
Determining the value of the gap may be a simple test for checking the consistency of the present theory. If the gap is typically comparable to the transition temperature, we should roughly observe the pair hopping with $J \sim k_B T_c/0.410$. If $T_c$ is approximately 100 K, $J$ should be approximately 24 meV. This value is within reasonable range for the two-body effective interaction, which is derived as a charge fluctuation. On the other hand, $J_z$ and $D$ for diagonal elements of the effective model can have larger values without the electrostatic breakdown of vacuum or the insulating barrier layer between superconducting layers, e.g., Fe$_2$As$_2$.

Here, note that an $S_z = 1$ state corresponds to any state with an extra pair in a layer, which may have multiple-colored states distinguished from each other. We only need to count the number of pairs that comes in or leaves a layer. If we consider states with many pairs coming in (or many vacancies leaving) a layer, we may utilize a higher-spin Heisenberg chain model. However, we know that Haldane gap decreases with increasing integer $S$. Thus, a high-temperature superconductor should be searched in a layered material, which can be mapped to an $S = 1$ model. One might find that the above discussion is easily applied to triplet superconductors in layered materials, when inter-triplet-pair Coulomb fluctuation is taken into account.

4. Density Functional Variational Theory

Recently, the author has proposed a theory of the model space in the multireference density functional theory. In this formulation, we use a new variational principle for the electron models defined by the density functional theory. A version of the density functional variational theory is given by the inequality

$$E_0 \leq \min_{X_i, \varepsilon_i, g_i} \left\{ \min_{\Psi} \bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] + \Delta \bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] \right\},$$

where $E_0$ is the ground-state energy of the electron system, and $\Psi$ inserted in $\Delta \bar{E}_{X_i, \varepsilon_i, g_i}[\Psi]$ is the minimizing $\Psi$ of the functional $\bar{G}_{X_i, \varepsilon_i, g_i}[\Psi]$. The energy functional determining the model is given as

$$\bar{G}_{X_i, \varepsilon_i, g_i}[\Psi] = \langle \Psi | \hat{T} + \hat{V}_{X_i} | \Psi \rangle + \frac{e^2}{2} \int d^3r d^3r' \frac{n_\Psi(r)n_\Psi(r')}{|r-r'|}$$

$$+ E_{\varepsilon_i}[n_\Psi] + E_{g_i}[\Psi] + \int d^3r v_{ext}(r)n_\Psi(r).$$

Here, $E_{\varepsilon_i}[n]$ is an LDA energy functional, which may be a GGA energy functional, and $E_{g_i}[\Psi]$ is a nonlocal correction parameter used in a standard DFT model. $E_{g_i}[\Psi]$ may be written by projection operators using a separable pseudo potential technique, an ultra-soft pseudo-potential technique, and a projector augmented wave technique. We introduced an energy difference functional as

$$\Delta \bar{E}_{X_i, \varepsilon_i, g_i}[\Psi] = \frac{e^2}{2} \int d^3r d^3r' \frac{1}{|r-r'|} \langle \Psi : (\hat{n}(r) - n_\Psi(r))(\hat{n}(r') - n_\Psi(r')) : | \Psi \rangle$$

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The proof of eq. (33) is easily realized by noting the next inequality

\[ \Delta E_{X,\epsilon,g}[\Psi] = F[n_\Psi] - \frac{e^2}{2} \int d^3r d^3r' \frac{n_\Psi(r)n_\Psi(r')}{|r - r'|} - E_{\epsilon_i}[n_\Psi] - \min_{\psi' \rightarrow n_\Psi} \left\{ \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} + E_{g_i}[\psi'] \right\} \]

\[ = \frac{e^2}{2} \int d\lambda \int d^3r d^3r' \frac{1}{|r - r'|} \langle \Psi_{\lambda,n_\Psi} : (\hat{n}(r) - n(r))(\hat{n}(r') - n(r')) : |\Psi_{\lambda,n_\Psi} \rangle \]

\[ - E_{\epsilon_i}[n_\Psi] - \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} - E_{g_i}[\psi'] \]

\[ \leq \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} - \frac{e^2}{2} \int d^3r d^3r' \frac{n_\Psi(r)n_\Psi(r')}{|r - r'|} \]

\[ - E_{\epsilon_i}[n_\Psi] - E_{g_i}[\psi'] - \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} \]

\[ = \langle \psi'|\tilde{V}_{\text{red}}\rangle_{\psi'} - \Delta E_{X,\epsilon,g}[\Psi]. \] (36)

Here, we used

\[ \min_{\psi' \rightarrow n_\Psi} \left\{ \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} + E_{g_i}[\psi'] \right\} = \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} + E_{g_i}[\psi], \] (37)

since the minimizing $|\psi'|$ of the above expression for the charge density $n_\Psi(r)$ is obtained by minimizing a functional,

\[ \hat{G}_{n_\Psi}[\psi'] = \langle \psi'|\tilde{T} + \tilde{V}_{\text{red}}\rangle_{\psi'} + \frac{e^2}{2} \int d^3r d^3r' \frac{n_\Psi(r)n_\Psi(r')}{|r - r'|} \]

\[ + E_{\epsilon_i}[n_\Psi] + E_{g_i}[\psi'] + \int d^3r v_{\text{ext}}(r)n_\Psi(r). \] (38)

which is given by $|\psi|$. We again find importance of the self-consistency in the minimizing process of $\hat{G}_{X,\epsilon,g_i}[\Psi]$.

Thus,

\[ E_0 \leq \min_{X,\epsilon,g_i} \left\{ \min_{\psi} \hat{G}_{X,\epsilon,g_i}[\psi] + \Delta E_{X,\epsilon,g_i}[\psi] \right\} \]

\[ \leq \min_{X,\epsilon,g_i} \left\{ \min_{\psi} \hat{G}_{X,\epsilon,g_i}[\psi] + \Delta E_{X,\epsilon,g_i}[\psi] \right\}. \]

Thus, we can start from a known LDA functional to construct a variational model of the electron system. The fluctuation term $\tilde{V}_{X_i}$ is formed by static two-body correlation functions,
which yield two-body effective interactions in the MR-DFT model. Thus, we have a firm ground for a beyond-LDA approach, considering that relevant fluctuation modes are inserted in the variational model. We may utilize GGA in place of LDA under the assumption that the exchange-correlation potential is always given in the simulation process.

In the density functional variational theory (DFVT), a simulation for determining the fluctuation term \( \langle \Psi | \hat{V}_X | \Psi \rangle \) is given, when a differentiable \( E_{\epsilon_i}[n] \) and/or an explicit \( E_g[\Psi] \) are prepared. Then, we always have a defined one-body part of the effective Hamiltonian in a self-consistent determination process of the self-consistent solution of the model. Thus, an LDA or GGA solution can be used to construct a correlated electron model of superconductivity. The model has effective two-body interaction terms. According to the model Hamiltonian, we can apply any appropriate solver for an effective many-body problem. Self-consistency is imposed by calculating the charge density, which redefines the exchange-correlation potential. Two-body processes and their interaction parameters are determined, so that they reduce the variational energy of the Coulomb system. The variational energy is given by evaluating all the terms in eqs. (33) and (35). At present, realistic determination processes are computationally demanding, but a preliminary simulation of \( \text{Sr}_2\text{CuO}_3 \) indicates that an optimization process indeed works for determining an effective interaction parameter. In this one-dimensional copper oxide with the \( d^9 \) configuration at each Cu, the on-site Hubbard interaction \( U > 0 \) is determined by searching the minimum variational energy.

5. Conclusions

We proposed a pair-hopping mechanism expected in a layered superconductor on the basis of MR-DFT. The definition of the effective model for a superconductor is given from the first-principles method. Determination techniques of the model is given by DFVT. The derived effective pair-hopping model suggests the realization of a valence-bond-solid state of an effective \( S = 1 \) Heisenberg anti-ferromagnetic spin chain. A bulk superconducting phase becomes gapped in the charge fluctuation mode.

Sufficient conditions for the pair-hopping mechanism are summarized as follows: (i) There is a two-body pair hopping process between layers, which may be direct or indirect. (ii) Inter-layer single-particle tunneling is negligible compared with the two-body pair hopping between layers. (iii) A correlation effect in a layer suppresses multiple-pair hopping at the same time, keeping the local charge neutrality and allowing minimum charge fluctuation in a uniform bulk superconducting state. These conditions allow us to have a high-temperature superconductor. The realization of the mechanism in iron arsenides is expected because we obtain (1) experimental observation of high-temperature superconductivity, (2) the two-dimensional electronic state given by GGA, and (3) the present formulation of the pair-hopping mechanism in MR-DFT. DFVT suggests that, if competing diagonal orders in magnetic and non-magnetic channels are not comparable in variational energy, the superconducting state is selected. For
the off-diagonal superconducting order, there is energy reduction in Coulomb energy, because the pair-hopping mechanism selects the unique ground state with the Haldane gap.

The importance of the interlayer pair tunneling process has often been stressed for cuprate high-temperature superconductors. In our DFVT, we can also derive a strategy for enhancing the stability of the superconductivity using our microscopic effective model. The Coulomb-originated pair hopping is derived via the charge fluctuation modes. One possible form is given by eq. (5). Here, we need to consider the sign of the superconducting order parameter. We have two contributions, namely, a \( \hat{Y} \)-process and a \( \hat{Z} \)-process, due to the appearance of two operators. The important point is that the sign of these processes are different. Depending on the two-dimensional superconducting order parameter, one of them can be effective for direct pair hopping. As for the super pair tunneling mechanism, the combination of the \( \hat{Y} \)-process and \( \hat{Z} \)-process may appear in the higher-order pair hopping process from one layer to another layer.

In Fig. 2(a), we show a possible scattering process from one layer to another layer. By using a \( \hat{Y} \)-process, two branches of the gap function, \( i.e. \), an \( m \)-th band with a positive sign and another \( m' \)-th band with a negative sign may be stabilized. In a \( \hat{Z} \)-process, the final pair potential does not need to change the sign from the initial one. The momentum conservation at a scattering center holds. According to this rule, we can find out relevant scattering processes depending on the geometry of the Fermi surfaces and the sign of the local order parameter \( \bar{\Delta}_{jj'}l \). Two examples shown in Fig. 2 are for (b) an extended \( s \)-wave state modeling iron arsenides and (c) a \( d \)-wave state for cuprates. The strength of these processes is dependent on the orbitals \( \phi_{jl} \) and effective coupling strength, and thus on the material structure considered. Furthermore, we need a strong superconducting fluctuation in a two-dimensional layer. For the enhancement of the intralayer fluctuation, we may rely on our knowledge of the spin-fluctuation mechanism of high-temperature superconductivity. Another known fact in the literature supporting the present pair-hopping mechanism is the electronic band structure calculations for optimally doped LaFeAsO, which has a higher \( T_c \) than NaFeAs. The two-dimensionality of Fermi surfaces is confirmed, when the experimentally observed lattice structure is assumed in the simulation or when hole doping is assumed in a theoretically determined lattice structure. A perfect two-dimensionality of the LDA or GGA band structures means a strong suppression of interlayer single-particle hopping processes as well as the appearance of correlation effects in each layer. The indirect pair tunneling mechanism further suggests the co-existence of magnetic order in an independent part of the layered superconducting system. If the magnetic structure only acts as a medium supporting the pair hopping processes, the gap formation in a stack of local superconducting two-dimensional electron systems is expected.

A simple comment on another attempt to elucidate a superconductivity is given for
pedagogical reason. The present pair hopping mechanism is allowed only for the interlayer pair scattering due to the Coulomb repulsion between electrons. If there is an effective attractive interaction at an attractive center between layers, the transition temperature vanishes, since the pair hopping is blocked. The existence of an on-site static attractive interaction coming from the Coulomb repulsion has been already disproved.\(^{53}\)

Finally, three possible comments on real superconductors are given as follows. The origin of inter-layer scattering processes relevant to bulk superconductivity may be the electron-phonon interaction as well as the intra-layer effective attraction. In the case of MgB\(_2\),\(^{54}\) the pair-hopping mechanism can give some amount of stabilization through the appearance of a hidden order parameter. Since we need to specify details of scattering processes that stabilize the Coulombic electron system, further theoretical investigation might be necessary.

For the realization of the effective \(S = 1\) Heisenberg model, we conjectured that a semimetallic band structure is favorable. Pseudo-electron-hole symmetry corresponds to the XXZ Heisenberg chain with the \(D\) term. To have the most stable Haldane gap, we also need to perform numerical simulation of a generalized Heisenberg chain model. Although a detailed discussion on the stability of the multiple-ordered state proposed on the basis of the present pair-hopping mechanism is required to determine the best condition by first-principles simulation, we expect to obtain a reliable estimator of \(T_c\) in the near future, since the numerical accuracy for the determination of the Haldane gap is now going beyond single precision.\(^{44}\)

In several cuprate superconductors, the realization of microscopic Josephson junction arrays is known to be related to the Josephson plasma.\(^{55-58}\) For the microscopic analysis of this phenomenon, the determination of the sign and structure of the superconducting order parameter is important. A simulation based on DFVT is expected to solve this problem, too.

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Fig. 1. Minimal model of the high-temperature superconductivity in a layered material. (a) In the layered superconductor, a Cooper pair may hop via a two-body pair-hopping process into the next layer, but single-electron tunneling processes are suppressed. (b) Extra pairs and resulting vacancies may be created by the hopping process with charge fluctuation. (c) Neighboring pairs or neighboring vacancy layers are energetically forbidden. Thus, we have a hidden string order in the Haldane phase.
Fig. 2. (a) Effective interaction process for the pair hopping from one layer to another layer. In the first \(l\)-th layer, a Cooper pair experiencing a positive pair potential is scattered into the next \(l'\)-th layer by a \(\hat{Y}\)-process, where the final state may be affected by a negative pair potential. In the scattering process, an electron with \((m, k, l, \sigma)\) of a pair is scattered into \((m', k', l', \sigma)\) with a momentum shift and another electron \((m, -k, l, -\sigma)\) of the pair obtains an inverse momentum shift to be \((m', -k', l', -\sigma)\). (b) Schematic viewgraph of the superconducting order parameter in the two-dimensional first Brillouin-zone of a model two-band superconducting state. If the Fermi surfaces are separated into a center one and another one around the \(M\) point, an extended \(s\)-wave state may be created. The interlayer pair hopping from the \(l\)-th center Fermi surface to the \(l'\)-th Fermi surface around \(M\) may occur. (c) A schematic viewgraph representing the sign of the order parameter for a model superconducting state with a \(d\)-wave state.
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