Phase diagram of high-temperature superconducting cuprates and pnictides

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Abstract. Phase diagram of high-temperature superconducting cuprates and iron pnictides is considered based on the theory emphasizing that the electronic state of superconductors can be described by the composed fermions. The theory is constructed with the Hamiltonian so modified by the unitary transformation as to apply the mean field approximation. It is indicated that the phase diagram of these superconductors can be explained from the viewpoint unifying the electronic states of superconducting cuprates and pnictides. The issues relevant to exotic phases are also discussed.

1. Introduction

Though there has been much study about high-temperature superconductors such as cuprates etc, its microscopic understanding still remains an insufficient stage [1-8]. Recently, the author proposed a unified theory to explain generally the properties of high-temperature superconducting cuprates and iron pnictides [9]. The theory is based on the extended \(d'-p\) model emphasizing that the electronic state of superconductors can be described by the composed fermions constructed with \(d-p\) operators, and is indicated to provide a universal explanation about the superconducting and normal properties of these superconductors. In this paper the phase diagrams of high-temperature superconducting cuprates and iron pnictides will be investigated and then evaluated comparing with the experimental facts.

2. Basic equations

The Hamiltonian is assumed to be an extended \(d'-p\) model for a single layer of square planar

\[
H = \sum_{i} \varepsilon_{i}^{\uparrow} d_{i}^{\dagger} d_{i} + \sum_{j} \varepsilon_{j}^{\uparrow} p_{j}^{\dagger} p_{j} + \sum_{j} \sum_{\langle i,j \rangle} (\varepsilon_{i}^{\uparrow} d_{i}^{\dagger} p_{j} + \text{H.c.}) + \sum_{\langle i,j \rangle} U_{i}^{\uparrow} d_{i}^{\dagger} d_{j} d_{j} d_{i} + \sum_{\langle i,j \rangle} V_{i,j} d_{i}^{\dagger} d_{j}^{\dagger} p_{j}^{\dagger} p_{i} \quad (1)
\]

where the operator \(d_{i}^{\dagger}\) creates electrons or holes of \(n\)-th M (Cu or Fe) 3\(d\) orbital at site \(i\), \(p_{j}^{\dagger}\) creates \(l\)-th L (oxide or pnictide) \(p\) electrons or holes at site \(j\), \(\varepsilon_{i} = 0\), and \(\varepsilon_{i}^{\uparrow}\) is the nearest-neighbor hopping integral. \(U_{i}^{\uparrow}\) and \(U_{i,j} (n \neq m)\) are the Coulomb repulsion and Hund coupling at M site, respectively, and \(V_{i,j}\) is the interaction between neighboring M and L sites. In (1), the vacuum is defined as M \(d'\) and L \(p\) states (\(x = 10, y = 6\) in the cuprate, \(x = 6, y = 6\) in the pnictide). Considering the \(d-p\) covalency effect, the operator combining the L states around M ion is defined as

\[
\vec{p}_{\text{site}} = \sum_{j \langle i \rangle} \varepsilon_{i,j}^{\uparrow} p_{j}^{\dagger} \quad \varepsilon_{i,j} = \sqrt{\sum_{j \langle i \rangle} \varepsilon_{i,j}^{\uparrow}} \quad (2)
\]
where \( j = i + x_i \) and \( x_j \) presents the directions of M-L bonding. Since the relation of \( \sum_j P_{ip}^* P_{jp} = N \sum_j \tilde{p}_{iij} \tilde{p}_{jj} \) (\( N \) is the valence ratio of \( d \) to \( p \)) is satisfied in the M-L compounds, Hamiltonian (1) is so changed as

\[
H = N \sum_{i, \sigma} \epsilon_{\sigma} \tilde{p}_{iij} \tilde{p}_{jij} + \sum_{i, \sigma} \left( \epsilon_{\sigma} d_{i\sigma}^+ \tilde{p}_{iij} + \text{H.c.} \right) + \sum_{i, \sigma} U_{ji\sigma} d_{i\sigma}^+ d_{i\sigma} d_{j\sigma}^+ d_{j\sigma} + N \sum_{i, \sigma} V_{i\sigma} d_{i\sigma}^+ d_{i\sigma} \tilde{p}_{iij} \tilde{p}_{jij}.
\]

(3)

Since the operator \( \tilde{p}_{iij} \) is not orthogonal between the neighboring M sites, it does not exactly satisfy anti-commutation relations. However it is approximated here that \( \tilde{p}_{iij} \) can be well-defined fermion operator.

To the second order in perturbation theory on the condition of \( \epsilon_{d \sigma} < U_{\alpha} (= U_{\sigma}) \), let us find out the effective Hamiltonian of Eq. (3). For simplicity, Hund coupling and the interaction between different 3\( d \)-orbitals are neglected. First in the second term of Eq. (3), the terms acting on the interaction \( U_{\alpha} \) as a perturbation can be selected as follow as

\[
H' = \sum_{i, \sigma} \left[ \epsilon_{\sigma} \left( n_{\sigma} d_{i\sigma}^+ \tilde{p}_{iij} (1 - n_{\sigma}) + (1 - n_{\sigma}) d_{i\sigma}^+ \tilde{p}_{iij} n_{\sigma} \right) \right] + \text{H.c.}
\]

(4)

where \( H' \) indicates the terms in the presence of fermions with the opposite spin at either \( d \) or \( p \) sites because the ground state is not assumed here to include the double occupancy states. Further, let us average the occupancy factors such as \( (1 - n_{\sigma}) \) by using \( \left\langle 1 - n_{\sigma} \right\rangle \). The Coulomb interaction \( U_{\alpha} \) in the ground state can be effectively eliminated from the starting Hamiltonian because double occupancy states at \( d \)-sites are inhibited by Coulomb repulsion. Considering the second term except \( H' \), Hamiltonian (3) is thus modified by

\[
H = N \sum_{i, \sigma} \epsilon_{\sigma} \tilde{p}_{iij} \tilde{p}_{jij} + \sum_{i, \sigma} \left\langle \left( 1 - n_{\sigma} \right) \left( \epsilon_{\sigma} d_{i\sigma}^+ \tilde{p}_{iij} + \text{H.c.} \right) \right\rangle + N \sum_{i, \sigma} V_{i\sigma} d_{i\sigma}^+ d_{i\sigma} \tilde{p}_{iij} \tilde{p}_{jij}
\]

\[+
\sum_{i, \sigma} \left( \left\langle 1 - n_{\sigma} \right\rangle \left\langle n_{\sigma} \right\rangle + \left\langle n_{\sigma} \right\rangle \left\langle 1 - n_{\sigma} \right\rangle \right) \left( J_1 d_{i\sigma}^+ d_{i\sigma} \tilde{p}_{iij} - J_2 d_{i\sigma}^+ \tilde{p}_{iij} d_{i\sigma} \right)
\]

(5)

where \( J_1 = \epsilon_{\sigma} (U_{\alpha} - N \epsilon_{\sigma} - N V_{\sigma}) \), \( J_2 = \epsilon_{\sigma} (N \epsilon_{\sigma} - N V_{\sigma}) \). Though the former part of the forth term in (5) corresponds to the kinetic energy due to the hopping between sites, it is neglected here due to the second order kinetic energy. The latter part corresponds to the effective anti-ferromagnetic interaction between \( d \)-fermions. Thus, the effective Hamiltonian is finally obtained as

\[
H_{\text{eff}} = N \sum_{i, \sigma} \epsilon_{\sigma} \tilde{p}_{iij} \tilde{p}_{jij} + \sum_{i, \sigma} \left\langle \left( 1 - n_{\sigma} \right) \left( \epsilon_{\sigma} d_{i\sigma}^+ \tilde{p}_{iij} + \text{H.c.} \right) \right\rangle + N \sum_{i, \sigma} V_{\sigma} d_{i\sigma}^+ d_{i\sigma} \tilde{p}_{iij} \tilde{p}_{jij}
\]

(6)

where \( V = V_{\sigma} + N \epsilon_{\sigma} V_{\sigma} \) : Coulomb interaction between the nearest neighboring sites in (1), \( V_{\sigma} \) : anti-ferromagnetic interaction \( V_{\sigma} = -\left( \left\langle 1 - n_{\sigma} \right\rangle \left\langle n_{\sigma} \right\rangle + \left\langle n_{\sigma} \right\rangle \left\langle 1 - n_{\sigma} \right\rangle \right) J_1 \), \( \sigma \neq \sigma' \).

Now the ground state of effective Hamiltonian (6) will be generally considered in two states depending on the doping conditions. One of these is the states in the neighborhood of the insulator (so-called Mott insulator) and the other is the superconducting state based on the band picture. First let us consider the region in the neighborhood of the insulator. The effective Hamiltonian (6) is appropriate in this case because its representation in real space is very useful in the treatment of this region. In order to enable to apply the mean field approximation, the operators \( d_{\sigma}^+ \tilde{p}_{iij} \) are changed by unitary transformations of

\[
b_{\sigma}^i = \alpha_{\sigma} d_{\sigma}^i + \beta_{\sigma} \tilde{p}_{iij}, \quad c_{\sigma}^i = \beta_{\sigma} d_{\sigma}^i - \alpha_{\sigma} \tilde{p}_{iij}, \quad \alpha_{\sigma}^2 + \beta_{\sigma}^2 = 1
\]

(7)

where \( b_{\sigma}^i, c_{\sigma}^i \) are defined as the mixing operators of M and L fermions. For the condition of \( \alpha_{\sigma} \beta_{\sigma} N \epsilon_{\sigma} = \left( 1 - n_{\sigma} \right) \epsilon_{\sigma} (\beta_{\sigma}^2 - \alpha_{\sigma}^2) \), the Hamiltonian (6) is transformed into
\[
H = N \sum_{\alpha \nu} \epsilon_\nu (\beta^\dagger \alpha - \alpha^\dagger \beta) (\beta^\dagger \beta_\nu b_{\alpha \nu} - \alpha^\dagger \alpha^\dagger \beta_\nu c_{\alpha \nu}^\dagger) + N \sum_{\alpha \nu} V(\alpha^\dagger \beta^\dagger \beta_\nu b_{\alpha \nu} \beta^\dagger + \alpha_\nu^\dagger \beta_\nu c_{\alpha \nu}^\dagger \beta^\dagger) + \beta^\dagger \alpha^\dagger \beta_\nu c_{\alpha \nu}^\dagger \alpha^\dagger \beta^\dagger c_{\alpha \nu}^\dagger \beta_\nu c_{\alpha \nu}^\dagger \beta^\dagger + \cdots \tag{8}
\]

Notice that the indexes \( n, l \) of \( \alpha_\alpha, \beta_\beta, b_\beta^\dagger, c_\alpha^\dagger, \) etc are omitted to avoid the complex representation. Since there appear many interaction terms in the transformed Hamiltonian (8), this transformation might make the problem somewhat difficult. However, the mixing of \( d \) and \( p \) fermions can be directly built in this Hamiltonian, which consists of two free fermions and the interaction terms between them. As a result this treatment has an advantage to enable to apply the mean field approximation because of the explicit representation of free fermions and their interaction terms. Next let us consider the case of the superconducting state based on the band picture. Since the representation in momentum space is appropriate in this region, the effective Hamiltonian of (6) is transformed into

\[
H = \sum_{k, \sigma} \epsilon_{\sigma} p_{\sigma k}^l p_{\sigma k}^* + \sum_{k, \sigma} \left( 1 - n_{\sigma} \right) \epsilon_{\sigma} s_{\sigma}(k)(-id_{\alpha k}^l p_{\sigma k}^l + ip_{\sigma k}^l d_{\nu k}) + N^{-1} \sum_{\lambda, \alpha, k, \nu} V_\alpha(\epsilon_{\alpha} \sigma) d_{\nu k}^l d_{\nu k}^* p_{\nu k}^l p_{\nu k}^* \tag{9}
\]

Here \( s_{\sigma}(k) = \sum_{\nu}(e_{\nu}^r e_{\nu}^l)^{\dagger} \exp(\imath k \cdot \mathbf{r}_\nu) \), \( \epsilon_{\alpha} \sigma = \sum_{\nu}(e_{\nu}^r e_{\nu}^l)^{\dagger} \exp(\imath k \cdot \mathbf{r}_\nu) \), \( \mathbf{r}_\nu(x, y) \) refers to the axis for the unit cell, and \( N \) is number of \( M \) sites in a single layer. The operators \( p_{\nu k}^l, d_{\nu k}^l \), which are Fourier transformation of \( p_{\sigma k}^l, d_{\sigma k}^l \), are reconstructed with fermion operators defined by unitary transformation

\[
b_{\sigma k}^l = \beta_{\sigma k}^l d_{\sigma k}^l + \imath \alpha_{\sigma k}^l p_{\sigma k}^l, \quad c_{\sigma k}^l = \beta_{\sigma k}^l d_{\sigma k}^l - \imath \alpha_{\sigma k}^l p_{\sigma k}^l, \quad \alpha_{\sigma k}^l + \beta_{\sigma k}^l = 1, \tag{10}
\]

where \( b_{\sigma k}^l, c_{\sigma k}^l \) satisfy anti-commutation relations. Notice that the operators \( p_{\nu k}^l, d_{\nu k}^l \) satisfy anti-commutator relations exactly, but those are approximated operators of \( \tilde{p}_{\sigma k}^l \) in momentum space. For the condition of \( \alpha_{\sigma k}^l, \beta_{\sigma k}^l = (1 - n_{\sigma}) \epsilon_{\sigma} s_{\sigma}(k)(\beta_{\nu k}^l - \alpha_{\nu k}^l) \), the Hamiltonian (9) is given by

\[
H = \sum_{k, \sigma} \sum_{\nu} \epsilon_{\nu} (\beta_{\nu k}^l - \alpha_{\nu k}^l) (\beta_{\nu k}^l b_{\sigma k}^l - \alpha_{\nu k}^l c_{\sigma k}^l) + N^{-1} \sum_{\lambda, \alpha, k, \nu} V_\alpha(\epsilon_{\alpha} \sigma) (\alpha_{\nu k}^l \beta_{\nu k}^l \beta_{\nu k}^l \beta_{\nu k}^l + \beta_{\nu k}^l \beta_{\nu k}^l \beta_{\nu k}^l \beta_{\nu k}^l + \beta_{\nu k}^l \beta_{\nu k}^l \beta_{\nu k}^l \beta_{\nu k}^l + \cdots)
\]

where the indexes \( n, l \) of \( \alpha_{\nu k}^l, \beta_{\nu k}^l, b_{\nu k}^l, c_{\nu k}^l \) etc are omitted to avoid the complex representation. Based on these effective Hamiltonians, the phase diagram of cuprate and pnictide superconductors will be considered in next chapters.

### 3. Cuprates
#### 3.1 Electronic state

The characteristics of cuprate superconductors is that it is a single \( d \)-band, \( p \)-band \( (n = 1, l = 1) \), superconductive in hole doping, and insulator in non-doping state. Though \( p \)-band is multi-orbitals, a single band of \( l = 1 \) will be only considered here. First let us consider the case of the nearly non-doped region. Assuming that there is no \( p \)-holes in half-filling, the relations of \( \{ 1 - n_{\sigma} \} \approx 0, \{ 1 - n_{\sigma} \} \approx (1 - 0.5 \delta) \) are derived. For the condition of \( 2n_{\sigma} \beta_{\sigma k}^l = (1 - 0.5 \delta) \alpha^l (\beta^l - \alpha^l) \), the Hamiltonian (8) is represented as

\[
H = 2 \epsilon_{\nu} (\beta^l - \alpha^l) (\beta^l b_{\nu k}^l - \alpha^l c_{\nu k}^l) + 2 \sum_{\nu} V(\alpha^l \beta^l b_{\nu k}^l b_{\nu k}^l + \alpha^l b_{\nu k}^l c_{\nu k}^l c_{\nu k}^l + \beta^l c_{\nu k}^l b_{\nu k}^l + \cdots) \tag{12}
\]

Here \( N_\nu \), the (valence ratio of \( d \) to \( p \)) = 2 and \( V + V(1 - 0.5 \delta)^{-1} \) \( (V_\nu \text{'s Coulomb interaction between the nearest neighboring sites, } V_\nu = \epsilon^l V \epsilon^l) \). For the parameters of cuprates, it will be selected that \( \epsilon^l = 0.5 \sim 1 \text{eV}, \epsilon^l = 1 \text{eV}, U = 5 \text{eV}, V_\nu = 1 \text{eV}, V_\nu = -1 \sim 2 \text{eV} \). It is well known that the ground state of superconducting cuprates shows antiferromagnets (so-called Mott insulator) in the non-doped
region [10,11]. Using the composite operators defined here, the non-doped wave function corresponds to
\[
|\Psi_{\text{mi}}\rangle = \prod_{i=1}^{N/2} (\alpha_i b_i^+ + \beta_i c_i^+) |0\rangle.
\]
where \( A \) or \( B \) shows the sub-space of antiferromagnetic lattice and \( N \) is number of Cu sites in a single layer. Since there exists no \( p \)-hole in half-filling Mott insulator, it will not be necessary to consider the interaction \( V \) in this case. However, in the existence of \( p \)-holes, since \( V_{\sigma\sigma'} \) is interpreted to be attractive due to \( d-p \) exchange antiferromagnetic interaction, the case of \( V < 0 \) will play an important role for determining the ground state. Considering the experimental facts that the doping can almost supply the \( p \)-holes, doping holes are expected to occupy the quantum state corresponding to this situation. For the condition \( \alpha^2 < \beta^2 \) which allows the reliable value of \( \varepsilon_i^c \) and \( \varepsilon_i^b \), the term \( b_i^+ c_{i'}^c, c_{i'}^c (c_i^c c_{i'}^b b_{i'}^c) \) can be the most dominant interaction. This means that \( b-c \) or \( c-b \) pair will mainly contribute to determine the ground state. Thus, for the equivalency of sites, the normalized wave function is assumed to be
\[
|\Psi_{\text{s}}\rangle = \prod_{i} (s + t b_i^c c_{i'}^c)(s + t c_i^c b_{i'}^c) |\Psi_{\text{mi}}\rangle \quad s^2(s^2 + t^2) = 1
\]
where the coefficient \( t \) indicates the probability of local-antiferro pair state. On the approximation using the relation of \( \langle \Psi_{\text{s}} | \sum p_i^a p_i^b |\Psi_{\text{s}}\rangle \approx 2Ns^2 t^2 = N\delta \) (\( \delta \): the doping ratio relative to half-filling), the ground-state energy is given by
\[
E_s = \langle \Psi_{\text{s}} | H |\Psi_{\text{s}}\rangle = N\delta (\varepsilon_i^c + V), \quad V < 0
\]
The energy of the excited states will be evaluated by using the presumed excited state wavefunction as follow as
\[
|\Psi_{\text{ex}}\rangle = \prod_{i} (s + t b_i^c c_{i'}^c)(s + t c_i^c b_{i'}^c) (\beta b_{i'}^c - \alpha c_{i'}^c) |\Psi_{\text{mi}}\rangle
\]
This is orthogonal to the ground state function and corresponds to breaking up a \( b-c \) (\( c-b \)) pair in \( i' \), the spin-up member going to \( b_{i'}^c, c_{i'}^c \). The excited energy is obtained as \( N\delta (\varepsilon_i^c + V) - 2V \). This indicates that there is the energy gap between the ground and the excited states. Thus, the wave function (14) will be identified as the pseudogap (PG) state in the nearly non-doped region. The PG energy is then estimated to be \( \Delta_p = |V| \) and the PG temperature \( T_p \) is approximated as the \( \lambda \Delta_p (\lambda < 1) \). What the excited state (16) indicates the creation of \( \tilde{p}_\sigma \) fermions is consistent with the experimental result that the PG in momentum space is only in the antinodal regions of the Brillouin zone, because the location of \( O \) ions correspond to the same regions in Brillouin zone. Notice that the wavefunctions \( |\Psi_{\text{s}}\rangle, |\Psi_{\text{ex}}\rangle \) are derived on the approximation that \( b_{i}^c \) and \( c_{i}^c \) satisfy anti-commutation relations. However, since these operators are not exactly orthogonal between neighboring Cu sites, Hamiltonian (12) has the matrix elements between the neighboring sites. This suggests that the states (14) and (16) will form the narrow bands reflecting the wavefunction overlap of the neighboring sites.

Next let us consider the case in the neighborhood of optimally doped region. In this doping region the relation of \( (1 - n_{\text{o}}) \approx 0, (1 - n_{\text{i}}) \approx 1 - 0.5\delta \) will be generally reasonable. On the condition of \( \alpha_i^c \beta_i^c \varepsilon_i^c = (1 - 0.5\delta)\varepsilon_i^c \), the Hamiltonian (9) is represented by
\[
H = \sum_{k} \varepsilon_k (\beta_k^c - \alpha_k^c)^{-1} (\beta_k^c b_{k^+}^c b_{k^+}^c - \alpha_k^c c_{k^+}^c c_{k^+}^c) + N^{-1} \sum_{\mathbf{k}, \mathbf{k}'} V(\mathbf{k}, \mathbf{k}) (\alpha_k a_k^c \beta_k^c b_{k^+}^c b_{k^+}^c b_{k^+}^c b_{k^+}^c b_{k^+}^c b_{k^+}^c + \alpha_k a_k^c \alpha_k b_{k^+}^c b_{k^+}^c c_{k^+}^c c_{k^+}^c + \beta_k b_{k^+}^c b_{k^+}^c b_{k^+}^c b_{k^+}^c c_{k^+}^c c_{k^+}^c + \beta_k b_{k^+}^c \alpha_k b_{k^+}^c c_{k^+}^c c_{k^+}^c + \cdots)
\]
where \( s(\mathbf{k}) = \sin k_x + \sin k_y \), \( \theta(\mathbf{k}, \mathbf{k}') = \cos(k_x - k_x') + \cos(k_y - k_y') \), and the Cu-O distance is used as the length unit. Here \( b'_s \) and \( c'_s \) satisfy anti-commutation relations. Note that \( V = V_\varepsilon + V_{c} \approx V'(1 - 0.5 \delta) < 0 \) because in this doping region the Coulomb interaction \( V_c \) can be neglected due to the screening effect of carriers. In (17) \( b'_s \) or \( c'_s \) fermion has the possibility of creating Cooper pairs, but \( b'_s \) will contribute to the Cooper formation because the Fermi surface exists in only \( b'_s \) band. Thus the BCS-like wave function is given by

\[
|\psi_s\rangle = \prod_{\alpha} (u_{\alpha} + v_{\alpha} b'_s b'_s) |0\rangle, \quad u_{\alpha}^2 + v_{\alpha}^2 = 1
\] (18)

Then, the gap equation is obtained as

\[
\Delta_\varepsilon = -0.5 \sum_{\alpha} \Delta_s V_{s\varepsilon} (\Delta_\varepsilon + \varepsilon_\varepsilon)^{-1/2}, \quad V_{s\varepsilon} = N^* V \alpha c_{s\varepsilon} c_{s\varepsilon} \theta_{s\varepsilon}.
\] (19)

where the relation \( \varepsilon_\varepsilon = 0.5(e^s + 4(1 - 0.5 \delta)^2 e^s(k) e^s(k')) - e_\varepsilon \) is defined, measuring the energy relative to the Fermi level \( e_\varepsilon \). Replacing the sum in gap equation by an integral, the solution which is even in \( \mathbf{k} \) is given by \( \Delta_\varepsilon = \Delta_0 \alpha \delta \theta_{\varepsilon} (c_{s\varepsilon} \cos k_y \cos k_y - \cos k_y \cos k_y) \). The solution decreasing the Coulomb interaction is \( \Delta_\varepsilon \propto (\cos k_y - \cos k_y) \) which agrees with the experimental fact about the anisotropic gap of high-temperature cuprate superconductors [12]. Thus \( \Delta_0 \) is determined by the relation

\[
1 = -0.5 \pi^{-1} V \alpha' \beta' (\cos k_x - \cos k_x) \cos k_y [\Delta_\varepsilon' \alpha' \beta' (\cos k_y - \cos k_y)^2 + \varepsilon_\varepsilon^{2}]^{1/2} d \mathbf{k}
\] (20)

Using several approximation on the band structure, the superconductive maximum gap energy and the ground-state energy are given by

\[
\Delta_\varepsilon = 2 e_\varepsilon \delta (1 + 4(1 - 0.5 \delta)^2 e^s l e^s) \exp(1 / N_e V),
\]

\[
E_\varepsilon = N \delta e_\varepsilon - N e_\varepsilon \delta (1 + 4(1 - 0.5 \delta)^2 e^s l e^s) \exp(21 / N_e V)
\] (21)

where \( N_e \) is the density of states at Fermi level and \( V = V_\varepsilon + V'(1 - 0.5 \delta) < (V' = eV / e^s) \). Denote that the energy relative to Cu 3d level is measured and the contribution of the \( c_{s\varepsilon} \) fermions to the total system energy is considered.

### 3.2 Phase diagram

The antiferromagnetic long-range order between copper sites disappears by holes doping, but there still exist the short-range order interaction which plays an important role in the presence of holes. As shown in the preceding section, the ground states in the neighborhood of the insulator and the superconducting region can be then calculated. However, the doping dependency of these states is not clear. There may be possible intermediate cases constructed with these mixed states. It will be then needed to consider the over-all phase diagrams. Now, an overall wavefunction is assumed to be

\[
|\psi(\delta)\rangle = f^{\delta_{p}} |\psi_{p}(\delta_p)\rangle + (1 - f)^{\delta_{s}} |\psi_{s}(\delta_s)\rangle.
\]

Here \( \delta_p, \delta_s \) are the doping quantity of PG and superconducting states and the total doping quantity \( \delta \) is defined to be \( \delta = f \delta_p + (1 - f) \delta_s \). The total free energy is then given by

\[
G = f E_p(\delta_p) + (1 - f) E_s(\delta_s), \quad (0 < f < 1)
\]

and the intermediate region is determined by minimizing \( G \) with respect to \( \delta, \delta_p, \delta_s \). Let us evaluate the doping quantity \( \delta_{p_m}, \delta_{s_m} \) by minimizing \( E_p(\delta_p) \) and \( E_s(\delta_s) \) and the minimum point of the total free energy in the condition of \( \delta_{p_m} < \delta_{s_m} \). As the case of \( \delta < \delta_{p_m} \) means \( \delta_p = \delta, \delta_s = 0 \), the system will show a pure PG state. At \( \delta = \delta_{p_m} \) superconductivity appears in the PG state and the mixed state will be maintained until the PG state disappear at the doping quantity \( \delta_{s_m} \) satisfying \( \delta = \delta_s \). In more increasing of \( \delta \) there exists a pure superconductor. Thus, the overall wave function will be represented as three regions of \( f = 1 (\delta < \delta_{p_m}), f = (\delta_{p_m} - \delta)(\delta_{p_m} - \delta_{s_m})^{-1} (\delta_{p_m} < \delta < \delta_{s_m}), \) and \( f = 0 (\delta > \delta_{s_m}) \), respectively. For both regions of \( \delta < \delta_{p_m} \) and
\( \delta_{pm} < \delta < \delta_{sm}, \Delta_p \) and \( T_p \) will decrease with increase of \( \delta \) and vanish at \( \delta = \delta_{sm} \). Since the superconductive region appearing at \( \delta = \delta_{pm} \) can be identified to be composed of very small superconductive region, the sufficient coherency to detect the net superconductivity will be less formed. Therefore, the superconductive state for \( \delta_{pm} < \delta < \delta_{sm} \) could be given by the effective gap \( \Delta_{eff} = (\delta - \delta_{pm}) (\delta - \delta_{sm})^4 \Delta_s (\delta_s) \). This also indicates that the superfluid density \( \delta_{sf} \) changes as \( \delta - \delta_{sm} \) in the region of \( \delta_{pm} < \delta < \delta_{sm} \). The superconductor will be the optimally doped state at the neighborhood of \( \delta = \delta_{sm} \), and in the over-doped region \( \Delta_s \) and \( T_s \) will decrease with \( \delta \) according to doping dependency. Thus, an overall phase diagram is theoretically obtained by considering three types of electronic states.

To reveal the reality of phase diagram, let us estimate \( \delta_{pm}, \delta_{sm}, \Delta_p(\delta_{pm}) \) and \( \Delta_s(\delta_{sm}) \) under the realistic values of system parameters such as \( v_p, e, V_c, |V_0|/\varepsilon \). Figure 1 (a), (b) show the dependency of \( \delta_{pm} \) and pseudo gap energy, and \( \delta_{sm} \) and superconductive gap energy on the \( d-p \) antiferromagnetic-like attractive interaction, respectively. Figure 1 (a) shows that for \( \varepsilon/v_p = 0.8 \) and \( |V_0|/\varepsilon = 1.5 \pm 0.2 \) \( (V_c = 1 \text{ eV}) \), \( \delta_{pm} = 0 \sim 0.1 \) and \( \Lambda_p(\delta_{pm}) = 0 \sim 200 \text{ meV} \). Similarly, Figure 1 (b) shows that for \( \varepsilon/v_p = 0.8, v_p = 1 \text{ eV}, |V_0|/\varepsilon = 0.8 \sim 1.2 \text{ eV}, \delta_{sm}=0.15 \sim 0.2, \Lambda_s(\delta_{sm}) = 1 \sim 10 \text{ meV} T_s(\delta_{sm}) = 3 \sim 30 \text{ K} \).

### 3.3 Exotic phases

Recently there has been much interest in various exotic phases of cuprates superconductors etc. [13]. Here let us discuss briefly the charge density wave (CDW), electron-nematic order and strange metal in normal state. First, it has been reported that CDW can coexist with superconductivity in underdoped region [14]. It has been confirmed that the observed CDW is static and short-range order. According to this paper, the state in underdoped region is constructed with PG and superconductive mixed phases, and the mixing state is evaluated by minimizing simply the free energy of these phases. However, more exactly, it is necessary to consider the space-like change of charge distribution due to the mixing of phases. Then, though PG ground state in mixing phase is not equivalent to CDW, it will possibly contain the charge order such as CDW. It has been also reported that the electron-nematic order can exist in the normal state of underdoped region [15]. Such orders have been interpreted as phases breaking the fourfold symmetry, which are translational invariant, but break rotational symmetry. The symmetry breaking suggests that the two oxygen ions in the copper-oxide unit are inequivalent. Since the electron-nematic order occurs in the PG phase, it may be related with the excited PG state. The reason is that there are the excitations of O holes in the excited PG state. Last let us discuss the strange metal. This has been discussed in the relation with quantum critical point (QCP) [13]. The strange
4. Pnictides

4.1 Electronic state

The characteristics of pnictide superconductors is that it is multi $d$ band, $p$ band ($n > 1, l > 1$) metal in non-doping, and superconductive in electron doping [16]. For the parameters of pnictides, it will be selected that $\varepsilon_v = \varepsilon = 0.1 \sim 0.3\,\text{eV}$, $\varepsilon_p = \varepsilon_p = 1\,\text{eV}$, $U = 2.5\,\text{eV}$, $V = 0 \sim 2\,\text{eV}$, $V' = -1 \sim 2\,\text{eV}$. Since the parent materials of pnictide are metal in non-doping, it seems to be appropriate to treat nearly non-doped region in the momentum representation. However, considering the antiferromagnetism (AFM) in non-doping, it is considered here to start from Eq. (8) in the real space presentation. The metallic state in nearly non-doped region can be interpreted to originate from the nonexistence of PG state due to the relation of $V = V + V' > 0$. This situation may correspond to the metallic state. In the momentum representation, $V_c$ can be neglected due to the screening effect of carriers, then $V \approx V' < 0$. In similarity with the cuprates, the superconductive gap equation derived from Eq. (9) is given by

$$$$
\Delta_{kn} = -0.5 \sum \Delta_{k, n} V_{k, n} (\Delta^i_{k, n} + \theta^i_{k, n})^{1/2}, \quad V_{k, n} = N^{-1} V_{k, n} \alpha_n \beta_k \beta^*_k \theta^n(k, k')$$

$$$$

Since Fe-3$d$ electrons are multi orbitals, it is needed to select the dominant orbitals of Fe contributing to superconductivity [17]. The orbitals of $d_{xz}$, $d_{yz}$ that have the strong hopping transition to the nearest Pn sites and intersect the Fermi surface are considered here. First let us consider the symmetry of superconductive paring wavefunctions [18]. The gap equation (22) is then considered in the case of two only orbitals $d_{xz}$, $d_{yz}$. For simplicity single $p$-orbital will be only considered. Considering that the square lattice of Fe$^{2+}$ is tetrahedrally coordinated with Pn anions $s_{\alpha}(k), s_{\beta}(k), \theta_{\beta}(k, k')$ and $\theta_{\beta}(k, k')$ are calculated as $s_{\alpha}(k) = \cos(k_x), s_{\beta}(k) = \cos(k_y), \theta_{\beta}(k, k') = \cos(k_x - k'_x), \theta_{\beta}(k, k') = \cos(k_y - k'_y)$ where the half of Fe-Fe distance is used as the length unit. In the case of $d_{xz}$ ($n = 1$), replacing the sum in (24) by an integral, the solution which is even in $k$ is given by $\Delta_{\Delta} = \Delta_{\alpha} \beta^* \cos_k$. Then, $\Delta_0$ is then determined by the relation similar with (19). The gap energy $\Delta_0$ is then obtained by solving the gap equation regarding $\Delta_0$. In the case of $d_{yz}$ ($n = 2$), using the transformations of $k_x \rightarrow k_x, \theta_\alpha \rightarrow \theta_\beta$, $\Delta_{\alpha} \rightarrow \Delta_{\beta}$, $\beta_\alpha \rightarrow \beta_\beta$, the similar gap equation is obtained. Since the band of $d_{xz}$, $d_{yz}$ are almost the same configuration, the value of $\varepsilon_1$ will be equal to that of $\varepsilon_2$. These indicates that the superconductive paring of Fe-Pn is $s$-like state different from the $d$-state of cuprates.

4.2 Phase diagram

Though some Fe-Pn materials exhibit low-temperature ($T_c \sim 4K$) superconductivity without doping, the high $T_c$ iron-based superconductors appear by a partial replacement of F$^-$ or H$^-$ ion at the oxygen site [19,20]. In general these iron-based superconductors indicate the phase diagram that the $T_c$ appears when the AFM disappear or weaken, and disappear with increasing of doping level. There are two phase diagrams of the 1111 and 122 system. For the 1111 system, the $T_c$ appears when ferromagnetism disappears. On the other hand, the AFM and superconductivity coexist in the 122 system. These phase diagrams can be explained in a similar way to the case of cuprates. In non-doping state, Fe ions are the superexchange antiferromagnetic state through the sites of pnictides that are non-magnetic materials (closed shell). However, it is recognized that there is the change from the closed shell state related to the mechanism of superexchange AFM. This means that the doped electrons will be supplied in Fe-3$d$ sites and the partial empty sites of pnictide. Therefore, in the similar situation with the case of cuprates, the doping will create the antiferromagnetic interaction contributing the superconductive state and reversely will weaken the superexchange antiferromagnetic interaction between Fe ions. Let us discuss the superconductive phases peculiar to iron pnictides. It has been reported that the doping by replacement of H$^-$ ion generally leads to the dome structure in phase diagrams of REFeAsO$_{1-x}$H$_x$.
(1111 system). The interesting thing is that the optimal doping level indicating the highest $T_c$ is decreased with decreasing the size of rare earth ion [21]. According to the theory, $T_c \propto \exp[-A/N_0 V(1-c\delta)^2]$. Since doping dependence of $T_c$ is determined by $V(1-c\delta)$, it will be needed to consider this variance relating with the size of RE ion. On the condition of fixed $V$ (d-p AF interaction), decreasing the ion size will weaken the correlation of fermions in the system. As a result, $V$ will be inclined to increase, and at the same time Fe-Fe AF interaction will weaken by carrier doping. Since the value of $V$ and $c$ increase with decreasing the size of RE ion, the optimal doping level decreases with increasing of $T_c$. Considering the above relations, the fitting curves of doping dependency of $T_c$ are shown in figure 2. Theoretical doping dependency of $T_c$ is consistent with the data of the highest $T_c$ in REFeAsO$_{1-x}$H$_x$ superconductors.

5. Conclusions
Phase diagrams of high-temperature superconducting cuprates and iron pnictides are investigated by extended d-p theory. In cuprates, PG and superconductive gap energy are evaluated, emphasizing on the minimum and optimal doping points in the superconductive state which are indispensable for determining the phase diagrams. It is then found that the phase diagram can be constructed with pure pseudo gap and superconductive states, and their mixed state. In pnictides, the phases constructed with the anti-ferromagnetism and superconductor can be explained in similar situation with the case of cuprates. The theory can also explains how the superconductive phases of REFeAsO$_{1-x}$H$_x$ change with the size of RE ion.

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