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Cooper-pair states for heavy fermions in the atomic representation: UPt_3

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The vertex equation for Cooper pairs of even or odd parity is developed in the Wannier representation taking into account the spin-orbit interaction of the periodic potential. We assume tightly bound d and f electrons and a short-range electron-electron interaction. The eigenvalue equation for the transition temperature T_c is reduced to a small set of coupled integral equations for the vertex eigenfunctions. These functions transform according to one and the same irreducible representation i_G of the crystal point group G, isomorphic to the factor group $\mathcal{G}/T_n$ ($\mathcal{G}$ = space group, T_n = group of primitive translations). The vertex functions depend on i_G and on the distance d between the two mates. The general symmetrization procedure is developed for the vertex function in the atomic representation or, equivalently, for the Cooper-pair orbitals. The application to the $5f$ orbitals of UPt_3 is presented for the contact pairs, the nearest-neighbor and the next-nearest-neighbor pairs. For all configurations, there are even- and odd-parity states by virtue of the inversion center between two U atoms in the *nonsymmorphic* lattice. The connection is established between the pair functions in the atomic representation and the Bloch representation used by other authors to study the $\mathbf{k}$-space symmetry of superconductivity in heavy-fermion metals. Thereby it is found that —in contrast to ^{3}He—the $\mathbf{k}$ dependence of the vertex functions is governed by the band structure and the periodic spin-orbit coupling.

I. INTRODUCTION

The theory of heavy-fermion superconductivity involves two basic problems. The first concerns the many-body effect governing the quasiparticle behavior and the pairing interaction, and the second involves the band-structure and spin-orbit-coupling effects determining the symmetry properties of the Cooper pairs. An answer to these questions may allow for a discussion of triplet (odd parity) versus singlet (even parity) superconductivity, a problem on which much of the recent work has centered. Because of the strong periodic spin-orbit (s.o.) coupling, the analogy between the superfluid properties of ^{3}He and heavy fermions, assumed in some theoretical papers, has no real justification. In particular, in ^{3}He the s.o. coupling occurs between the spin $\mathbf{S}$ and the angular momentum $\mathbf{L}$ of a pair of atoms, by virtue of a dipole-dipole interaction between two ^{3}He atoms. On the other hand, the ordinary one-electron s.o. potential affects the itinerant motion of a heavy fermion. The s.o. interaction between a pair of electrons caused by the e-e Coulomb interaction, the "spin-other orbit" interaction, is negligible in metals, as is well known from the paramagnetic relaxation in metals. The same is true for the effect of the phonon-modulated s.o. coupling on the pairing interaction, as compared with the ordinary Bardeen-Cooper-Schrieffer (BCS) interaction.

The heavy electrons occupy partly filled narrow bands spanned by the tightly bound f and d orbitals of the actinide (rare-earth) and transition-metal ions. The f and d electrons revolve several times around their atoms before the itinerant motion—in the case of f electrons by virtue of hybridization—carries them to a neighbor site. Hence, we assume for our discussion of the superconducting pair states that we can write "realistic" Bloch wave functions in terms of Wannier orbitals that have the proper site and spin-orbit symmetries.

Our first goal is to set up the transition-temperature equations that determine the possible instabilities of the normal phase against the Cooper-pair formation in narrow s.o. energy bands, assuming that the crystal has a center of inversion. Ignoring the s.o. interaction and assuming singlet pairing Appel and Kohn[1,2] have developed the theory of superconductivity in the site representation in order to discuss the atomic aspects of BCS superconductivity. Here, for the s.o. Cooper pairs, we set up the T_c eigenvalue equations for even- and odd-parity superconductivity. The symmetry of the kernel $\mathcal{K}$ is determined by the symmetry properties of the Cooper pairs formed from Wannier electrons which occupy either the same or the near-neighbor sites. The pair formation occurs as the temperature T approaches T_c from above. At T_c the vertex eigenfunction Γ satisfies the linear and homogeneous eigenvalue equation,

$$\Gamma = -\tfrac{1}{2}\Gamma GGI \, , \tag{1.1}$$

where G denotes the quasiparticle Green's function and I is the irreducible interaction between two electrons. In the Bloch ($\mathbf{k}$) representation, the symmetry properties of the eigenfunctions, solving for the homogeneous integral equation (1.1), are obtained and discussed by different authors, applying in a rigorous manner the double-group theory to singlet and triplet superconductors.[3-6] The actual evaluation of the pairing kernel, $\mathcal{K} = GGI$, is difficult in the Bloch representation due to the local character of d and f electrons and their short-range interaction with phonons and with magnetic excitations.[7] Hence, a suitable formulation of Eq. (1.1) for tightly bound s.o. electrons is developed here in the Wannier representation. This representation has been used with some success in previous papers to discuss BCS superconductivity in narrow d bands.[9] In Sec. II we proceed from Eq. (1.1) to discuss the general symmetry properties of the eigenfunctions Γ and the kernel $\mathscr{K}$. The general procedure for constructing the Cooper-pair orbitals in the atomic s.o. representation is developed in Sec. III, for the crystal symmetry of a *nonsymmorphic* lattice. The resulting pair orbitals are characterized by the distance d between the two mates and the irreducible representation i_G of the point group G that governs the symmetry behavior of the pair. In Sec. IV the theory is applied to $\mathrm{UPt_3}$ to obtain the pair states for the $5f$ orbitals at the U atoms. We assume that the two $5f$ mates reside at the same atom, at nearest- and at next-nearest-neighbor atoms. The vertex equation is discussed in Sec. V and it is shown that for each symmetry of a Cooper pair, characterized by i_G, we obtain a small set of coupled equations that determine the transition temperature T_c. Which vertex symmetry yields the highest value of T_c depends on the pairing kernel $\mathscr{K}$. Finally, in Sec. VI we establish the connection between the Cooper pairs in the atomic and in the Bloch representations, the latter being used by other authors[3-6] to discuss the $\mathbf{k}$-space symmetry of Cooper pairs near the Fermi energy. Because of the underlying band structure—including periodic spin-orbit coupling—it appears that the $\mathbf{k}$ dependence of the vertex eigenfunctions (or of the order parameter), in general, cannot be described in terms of simple $\mathbf{k}$ polynomials. In particular, the occurrence of certain irreducible representations depends on the details of the band structure at ϵ_F. A summary and an outlook conclude the paper.

II. VERTEX EQUATION AND THE SYMMETRY OF ITS EIGENFUNCTIONS

The vertex eigenfunction of Eq. (1.1) depends on the coordinates, spins, and frequencies of the two electrons that become a Cooper pair as $T \rightarrow T_c$ from above: $\Gamma = \Gamma(\mathbf{r}s,\mathbf{r}'s';\omega)$.[9,10] The Cooper-pair instability occurs for pairs of zero imaginary frequency, $\omega_1 = -\omega_2 = \omega$. We note that Γ has the same symmetry properties as the order parameter Δ with $T \rightarrow T_c$ from below.

The symmetry properties of Γ depend on the symmetry of the single-particle states. Because of the large s.o. interaction in the U atoms, the usual decomposition of Eq. (1.1) into two equations for spin-singlet and spin-triplet pairs is not possible. The eigenfunctions Γ can be classified according to the symmetry group of $\mathscr{K}$ of Eq. (1.1). Thus, the eigenfunctions transform according to an irreducible representation of the double group G.

The function Γ has the following symmetry properties.

Translational symmetry,

$$T_{\mathbf{n}}\Gamma = \Gamma(\mathbf{r}+\mathbf{n}s,\mathbf{r}'+\mathbf{n}s') = \Gamma(\mathbf{r}s,\mathbf{r}'s') \ , \tag{2.1}$$

where $T_{\mathbf{n}}$ is an element of the group of primitive translations, T_n.

Antisymmetry,

$$A\Gamma = -\Gamma(\mathbf{r}'s',\mathbf{r}s) = \Gamma(\mathbf{r}s,\mathbf{r}'s') \ . \tag{2.2}$$

Parity,

$$P\Gamma = \Gamma(-\mathbf{r}s,-\mathbf{r}'s') = \pm\Gamma(\mathbf{r}s,\mathbf{r}'s') \ . \tag{2.3}$$

Time reversal,

$$K\Gamma = ss'\Gamma^*(\mathbf{r}-s,\mathbf{r}'-s') \ , \tag{2.4}$$

as follows from Nozieres.[9]

Crystal-symmetry operations,

$$R\Gamma(\mathbf{r}s,\mathbf{r}'s') = \sum_{s_1,s_2} \Gamma(R^{-1}\mathbf{r},s_1;R^{-1}\mathbf{r}',s_2) \times D^{(1/2)}_{ss_1}(R) D^{(1/2)}_{ss_2}(R) \ , \tag{2.5}$$

where R is an element of the group G. We note that—ignoring primitive translations—the remaining elements of G do not form a group since the products of two such elements may be an element of T_n. As suggested by Herring[11] we consider G to be a group, associating the operations of T_n with the identity. In the following we use this extended definition of the identity, and take G to be a group, isomorphic to $\mathscr{G}/T_n$ and to the point group of the crystal. The matrix $D^{(1/2)}(R)$ is the rotational matrix for the two spin eigenfunctions $\delta_+(s)$ and $\delta_-(s)$, using the z direction as the axis of the spin quantization. The parity of Γ is conserved by virtue of the inversion symmetry. Therefore, it is convenient to fix the parity and to treat the two cases of even and odd parities separately.

The two-particle function $\Gamma(\mathbf{r}s,\mathbf{r}'s')$ can be written in terms of the products of single-particle functions, the symmetry of which is given by the periodic lattice Hamiltonian. We choose Wannier orbitals as the suitable single-particle wave functions. These functions are related to Bloch waves,

$$\psi_{\mathbf{k}\rho}(\mathbf{r}s) = \frac{1}{\sqrt{N}} \sum_{\mathbf{n},\tau} \sum_{i,\mu} e^{i\mathbf{k}\cdot(\mathbf{n}+\tau)} a_{i\mu,\tau}(\mathbf{k}\rho) w_{i\mu}(\mathbf{r}-\mathbf{n}-\tau,s) \ , \tag{2.6}$$

where the wave vector $\mathbf{k}$ incorporates the band index and ρ is the two-valued pseudospin of the Bloch state;[12] N is the total number of atoms in the crystal. The Wannier orbital $w_{i\mu}$, centered at the site $\mathbf{n}+\tau$, transforms according to the spin representation $\Gamma_i \equiv i$ of the double point group at the site τ. The index μ labels a basis function. The symmetry properties of the $\psi_{\mathbf{k}\rho}$ under the inversion J, K, and Blount's conjugation JK are discussed in Ref. 12. The Wannier orbitals are related to the Bloch waves,

$$w_{i\mu}(\mathbf{r}-\mathbf{n}-\tau,s) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\rho} e^{-i\mathbf{k}\cdot(\mathbf{n}+\tau)} a^*_{i\mu,\tau}(\mathbf{k}\rho) \psi_{\mathbf{k}\rho}(\mathbf{r}s) \ . \tag{2.7}$$

We assume canonical bands, that is, the symmetry of the Bloch waves associated with a band complex is determined by a particular orbital symmetry, e.g., d or f. The same holds for the Wannier orbitals. We assume "realistic" Bloch bands[13] in that the quasiparticle effects are contained in the expansion coefficients $a_{i\mu,\tau}$. These coefficients measure the weight of $w_{i\mu}$ in the Bloch state $\psi_{\mathbf{k}\rho}$.

The symmetry properties of $\psi_{\mathbf{k}\rho}$ remain unchanged by the quasiparticle effects. We emphasize this point because the single-electron band model may not be appropriate for describing the electronic states of solids with more than one f electron per atom and for intra-atomic Coulomb energies larger than or comparable with the band width.[14] The discussion of Herbst[15] of electron excitation energies in actinide metals supports the contention that the $5f$ electrons of the light actinides such as U are similar to the itinerant $3d$ electrons of the transition metals. Hence, the recent band-structure calculations for UPt_3, based on the local density approximation, yield pertinent insight into the d-f hybridization and the spin-orbit coupling effects.[16–19]

The vertex eigenfunction Γ is now expressed in terms of the Wannier orbitals $w_{i\mu}$,

$$\Gamma(\mathbf{r}s,\mathbf{r}'s';\omega)=\sum_{\mathbf{n}_1\tau_1,\mathbf{n}_2\tau_2}\sum_{i\mu,j\nu} w_{i\mu}(\mathbf{r}-\mathbf{n}_1-\tau_1,s) \times w_{j\nu}(\mathbf{r}'-\mathbf{n}_2-\tau_2,s')g(1,2;\omega)\ . \tag{2.8}$$

Here g denotes the vertex function in the Wannier representation where the two electrons occupy the orbitals $i\mu$ and $j\nu$ at the sites $\mathbf{n}_1+\tau_1$ and $\mathbf{n}_2+\tau_2$, respectively, e.g., $1=(\mathbf{n}_1,\tau_1,i\mu)$. For a Wannier pair, the eigenfunction g fulfills the equation,

$$g(1,2;\omega)=-\frac{1}{\beta_c}\sum_{\omega'}\sum_{1',2'} g(1',2';\omega')\langle 1',2';\omega' \,|\, \mathscr{K} \,|\, 1,2;\omega\rangle\ , \tag{2.9}$$

where the antisymmetrized kernel is given by

$$\langle 1',2';\omega' \,|\, \mathscr{K} \,|\, 1,2;\omega\rangle=\tfrac{1}{2}\sum_{1'',2''}[G(1',1'';\omega')G(2',2'';-\omega')\langle 1'',2'';\omega' \,|\, I \,|\, 1,2;\omega\rangle - G(1',2'';\omega')G(2',1'';-\omega')\langle 2'',1'';\omega' \,|\, I \,|\, 1,2;\omega\rangle]\ . \tag{2.10}$$

Here G is the one-particle Green's function in the Wannier representation and I is the irreducible interaction. The kernel $\mathscr{K}$ is invariant under the symmetry operations of G. Equation (2.9) has the general form of the vertex equation of the previous work on BCS superconductivity.[1,2]

In Sec. III we determine the linear combinations of the basic pairs, $w_{i\mu}(\mathbf{r},s)w_{j\nu}(\mathbf{r}',s')$, which transform according to an irreducible representation of G. Thereby, the vertex equation (2.9) is decomposed into a system of small sets of homogeneous equations. The symmetry properties of each set are characterized by an irreducible representation of G. In general, different representations will lead to different T_c's. It is the pairing interaction I contained in $\mathscr{K}$ that selects the symmetry of the pair orbital with the highest T_c.

III. SYMMETRIZED COOPER-PAIR ORBITALS

Starting from the basic pair orbitals, $w_{i\mu}w_{j\nu}$, we now construct the symmetrized orbitals which are invariant under G. Alternatively, starting from the basic vertex functions in the site representation, $g(1,2)$, we construct the symmetrized functions which transform according to an irreducible representation of G.

The symmetrized pair orbitals have the following properties: translational invariance, antisymmetry, parity, and crystal symmetry. The time-reversal invariance may or may not be broken. The main problem in constructing the symmetrized orbitals is to account for the crystal symmetry, that is, the proper and in proper rotations, some of which are accompanied by nonprimitive translations.

Taking into account the translational invariance, the vertex function is written as

$$\Gamma(\mathbf{r}s,\mathbf{r}'s')=\sum_{\mathbf{m},\mathbf{n}}\sum_{\tau_1,\tau_2}\sum_{i\mu,j\nu} \mathscr{f}g(\mathbf{n}+\tau_1,i\mu,\tau_2,j\nu)\ , \tag{3.1}$$

where the basic pair orbital is given by

$$\mathscr{f}\equiv w_{i\mu}(\mathbf{r}-\mathbf{n}-\mathbf{m}-\tau_1,s)w_{j\nu}(\mathbf{r}'-\mathbf{m}-\tau_2,s')\ . \tag{3.2}$$

The two mates are at the sites $\mathbf{m}+\mathbf{n}+\tau_1$ and $\mathbf{m}+\tau_2$ in the orbitals $i\mu$ and $j\nu$, respectively. In Eq. (3.1) g is the vertex function in the site representation; $\mathbf{n}=\mathbf{n}_1-\mathbf{n}_2$, $\mathbf{m}=\mathbf{n}_2$. The antisymmetry of Γ translates into

$$g(\mathbf{n}+\tau_1,i\mu;\tau_2,j\nu)=-g(-\mathbf{n}-\tau_2,j\nu;\tau_1,i\mu)\ . \tag{3.3}$$

If the vertex function is time-reversal symmetric, then

$$g(i\mu,j\nu)=\mu\nu g^*(i,-\mu;j,-\nu)\ . \tag{3.4}$$

On the right-hand side occurs Kramer's conjugate function, $g^*(-\mu,-\nu)$. Finally, when the symmetry element R of G operates on Γ, we have

$$R\Gamma=\sum_{\text{sites}}\sum_{\text{orbitals}} R[w_{i\mu}(\mathbf{r}-\mathbf{n}-\mathbf{m}-\tau_1,s) \times w_{j\nu}(\mathbf{r}'-\mathbf{m}-\tau_2,s')]g\ , \tag{3.5}$$

with the sites $\mathbf{m}$, $\mathbf{n}$, τ_1, and τ_2 and the orbitals $i\mu$ and $j\nu$; furthermore

$$Rw\cdot w=\sum_{\mu',\nu'} w_{i\mu'}[\mathbf{r}-R(\mathbf{n}+\mathbf{m}+\tau_1),s] \times w_{j\nu'}[\mathbf{r}'-R(\mathbf{m}+\tau_2),s'] \times D^{(i)}_{\mu'\mu}(R)D^{(j)}_{\nu'\nu}(R)\ . \tag{3.6}$$

By considering the equivalent point of view, R transforming g, and not $w_{i\mu}w_{j\nu}$ we get

$$R\Gamma=\sum_{\text{sites}}\sum_{\text{orbitals}} w_{i\mu}w_{j\nu}Rg\ , \tag{3.7}$$

where

$$Rg=\sum_{\mu',\nu'} g[R^{-1}(\mathbf{n}+\tau_1),i\mu';R^{-1}\tau_2,j\nu']\times D^{(i)*}_{\mu'\mu}(R^{-1})D^{(j)*}_{\nu'\nu}(R^{-1}) . \tag{3.8}$$

From the two alternatives, namely symmetrizing the pair orbitals $\mathscr{f}$ or the vertex eigenfunctions g, we choose the first one and proceed to find the linear combination of the $\mathscr{f}$'s which transform according to the irreducible representations of the group G.

A. Orbitals for a fixed pair of atomic sites

P is the point group of an atomic site. For a fixed *pair* of atomic sites, S is the group of symmetry operations which leave both of the two sites invariant. S is a subgroup of G. The representations i_S are determined by the compatibility relations with the representations i of the group P. We assume that both sites, $\mathbf{n}+\tau_1$ and τ_2, have the same point symmetry. Then, S is a subgroup of P. If the two sites are identical, we have $S=P$. The *one-electron orbitals* which are the basic functions of i_S are obtained from the compatibility relations between the representations i and i_S. The *pair orbitals,* invariant under S, transform according to the Kronecker products of the representations of S; they are given by

$$\mathscr{f}(\mathbf{r}s,\mathbf{r}'s';i_S\mu_S)=\sum_{\mu,\nu} C^{iji_S}_{\mu\nu\mu_S}A\,[w_{i\mu}(\mathbf{r}-\mathbf{n}-\tau_1,s)\times w_{j\nu}(\mathbf{r}'-\tau_2,s')] , \tag{3.9}$$

where μ_S denotes a basis function of $i_S=i_S\ (i,j)$ and where A is the antisymmetrization operator,

$$A=\frac{1-\mathscr{P}}{[2(1+\delta_{ij})]^{1/2}} ; \tag{3.10}$$

$\mathscr{P}$ is an operator that interchanges $\mathbf{r}s$ with $\mathbf{r}'s'$. The coupling coefficients C are obtained by the projection operator method. The inversion of Eq. (3.9) is straightforward and contains C^*.

In the special case where the two electrons occupy the Wannier orbitals $w_{i\mu}$ and $w_{j\nu}$ at one and the same site, $n=0$ and $\tau_1=\tau_2$, the representations i_S are readily found from the Kronecker product tables.

In general, for two *fixed* atomic sites, $\mathbf{n}+\tau_1\neq\tau_2$, the pair states invariant under S are given by Eq. (3.9). In addition to the elements of S, there may exist symmetry operations that leave the *pair of sites* $\mathbf{n}+\tau_1$ and τ_2 invariant, but which interchange the two sites. This group is called $\bar{S}$. The set product

$$\mathscr{S}=S\cdot\bar{S} \tag{3.11}$$

is isomorphic to a point group.

To construct the basis functions which transform according to the irreducible representations of $\mathscr{S}$, let us assume that $\bar{S}$ has two elements, namely the identity $\bar{S}_1$ and the operation $\bar{S}_2$ that interchanges the two sites $\mathbf{n}+\tau_1$ and τ_2. A case in point for the occurrence of $\bar{S}$ are the crystal structures of UPt_3 and UBe_{13}, where a center of inversion exists between two Uranium atoms: $\bar{S}_1=\{E,0\}$, $\bar{S}_2=\{J,\tau\}$, where the latter element produces an inversion J at the first site τ_1 followed by a nonprimitive translation τ which sends τ_1 into τ_2, cf. Fig. 1. The two symmetry operations $\bar{S}_1$ and $\bar{S}_2$ allow for the definition of the two pair orbitals

$$\mathscr{f}[(\mathbf{n}+\tau_1,\tau_2),\kappa;i_S\mu_S]=\bar{S}_\kappa\mathscr{f}(\mathbf{n}+\tau_1,\tau_2;i_S\mu_S),\quad \kappa=1,2 . \tag{3.12}$$

The term $(\mathbf{n}+\tau_1,\tau_2)$ implies that we are dealing with the basis orbitals at a given *pair of atomic sites.* In terms of these $\mathscr{f}$'s, the orbitals transforming according to $\mathscr{S}$ are given by

$$\mathscr{f}(\,|\mathbf{n}+\tau_1-\tau_2|\,,i_{\mathscr{S}}\mu)=\sum_{\kappa=1,2} C(i_S,i_{\mathscr{S}},\mu;\kappa)\mathscr{f}[(\mathbf{n}+\tau_1,\tau_2),\kappa;i_S\mu] . \tag{3.13}$$

For the even-parity states, $i_{\mathscr{S}}=i_S^+$, the coupling coefficients $C(\kappa)=1/\sqrt{2}$ for $\kappa=1,2$. For the odd-parity states, $i_{\mathscr{S}}=i_S^-$, the coupling coefficients are $+1/\sqrt{2}$ and $-1/\sqrt{2}$, respectively.

B. Construction of the cell orbitals

The symmetry operations which transform a given pair 1 into equivalent pairs, with their center of mass $\mathbf{m}$ in the same unit cell, form a group that we denote by T. This group is a subgroup of G,

$$G=\mathscr{S}\cdot T . \tag{3.14}$$

The cell orbitals transform according to the irreducible representations i_G of G.

First, let us consider the case where T is a point sym-

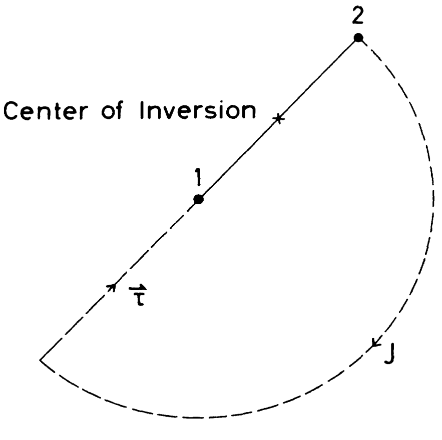

FIG. 1. The symmetry operation $\{J,\tau\}$. It consists of the inversion J followed by the nonprimitive translation τ. When $\{J,\tau\}$ is applied to site 1, 1→2, and 2→1.

metry group with the elements T_λ ($\lambda=1,2,\ldots,\lambda_0$). Applying the operations T_λ to pair 1, we produce new orbitals of the same intersite distance,

$$\mathscr{f}(d,\lambda;i_{\mathscr{S}}\mu_{\mathscr{S}})=T_\lambda\mathscr{f}(d,1;i_{\mathscr{S}}\mu_{\mathscr{S}}) , \qquad (3.15)$$

where $d=|\mathbf{n}+\tau_1-\tau_2|$ and λ labels the angular directions with respect to the pair 1 at $\mathbf{n}+\tau_1$ and τ_2.

The cell orbitals are the linear combinations of the $\mathscr{f}$'s, Eq. (3.15), which transform according to the representations i_G of G,

$$\mathscr{f}(d,i_G\mu_G)=\sum_{\lambda,\mu_{\mathscr{S}}} C(i_{\mathscr{S}}\mu_{\mathscr{S}},i_G\mu_G;\lambda)\mathscr{f}(d,\lambda;i_{\mathscr{S}}\mu_{\mathscr{S}}) , \qquad (3.16)$$

where μ_G denotes a basic function of i_G. The coupling coefficients C are found by projecting the basis set, $\mathscr{f}(\lambda)$, into a representation of i_G. To determine the projections we use the group properties of $\mathscr{S}\cdot T$, which can be a set product as shown in Appendix B.

The cell orbitals, Eq. (3.16), present the final form of the symmetrization procedure, provided $G=\mathscr{S}\cdot T$. Then, this product exhausts the symmetry elements of G. The cell orbitals can be written as

$$\mathscr{f}(d,i_G\mu_G)=\sum_{i\mu,j\nu}\sum_{\kappa,\lambda} C^{iji_G}_{\mu\nu\mu_G}\mathscr{f}(d,\lambda,\kappa;i\mu,j\nu) . \qquad (3.17)$$

The coupling coefficients $C\equiv C(\lambda,\kappa)$ are obtained from Eqs. (3.9), (3.13), and (3.16) as

$$C^{iji_G}_{\mu\nu\mu_G}=\sum_{i_S,\mu_S}\sum_{i_{\mathscr{S}},\mu_{\mathscr{S}}} C(i_{\mathscr{S}}\mu_{\mathscr{S}},i_G\mu_G;\lambda) \times C(i_S\mu_S,i_{\mathscr{S}}\mu_{\mathscr{S}};\kappa)C^{iji_S}_{\mu\nu\mu_S} , \qquad (3.18)$$

where the product of the three C's on the right-hand side reflects the three symmetrization steps (from left to right): symmetrization of the basic pair orbital for fixed atomic sites, parity symmetrization, and cell-pair construction.

In the second case, the set of equivalent pairs is obtained from the given pair 1 by the symmetry elements of the point group T and by the elements of a group $\overline{T}$ which contains nonprimitive translations. Hence, the elements of the group,

$$\mathscr{T}=T\cdot\overline{T} , \qquad (3.19)$$

when applied to the given pair 1 lead to the equivalent pair orbitals. Now, we have

$$G=\mathscr{T}\cdot S \qquad (3.20)$$

and proceed as in the first case to obtain the cell orbitals that transform according to the i_G's.

We conclude this section with the equations that give the transformations of the cell orbitals under a symmetry operation R and under the time-reversal operation K,

$$R\mathscr{f}(\mathbf{r}s,\mathbf{r}'s';d,i_G\mu_G)=\sum_{\mu'_G}\mathscr{f}(i_G\mu'_G)D^{(i_G)}_{\mu'_G\mu_G}(R) \qquad (3.21)$$

and

$$K\mathscr{f}(i_G\mu_G)=\sum_{\mu'_G}\mathscr{f}(i_G\mu'_G)D^{(i_G)}_{\mu'_G\mu_G}(-i\sigma_y) , \qquad (3.22)$$

where the rotation through an angle π about the y axis is a symmetry element of G: $C'_{21}=-i\sigma_y$. The transformation of the cell-vertex function g is given by

$$Rg(i_G\mu_G)=\sum_{\mu'_G} g(i_G\mu'_G)D^{(i_G)^*}_{\mu'_G\mu_G}(R^{-1})$$

and

$$Kg(i_G\mu_G)=\sum_{\mu'_G} D^{(i_G)}_{\mu_G\mu'_G}(-i\sigma_y)g^*(i_G\mu'_G) .$$

IV. 5f PAIR ORBITALS IN UPT$_3$

We now proceed to determine the cell orbitals for the 5f electrons in UPt$_3$. This compound has the nonsymmorphic space group, $\mathscr{G}=D^4_{6h}$. The primitive translations span the hexagonal structure, shown in Fig. 2. The crystal has two formula units per unit cell, Fig. 3. There is a center of inversion at the midpoint between the two U atoms which are connected by a nonprimitive translation τ. The point symmetry of each of the U atoms is given by the group D_{3h}, the twelve elements of which are: E the identity; $C_3^\mp$ the rotation through $\pm 2\pi/3$ about the z axis; C'_{21} the rotation through π about 3 axes within the x-y plane; $S_3^\mp$ the rotation through $\pm 2\pi/3$ followed by a reflection in the x-y plane; σ_h the reflection in the x-y plane; $\sigma_{v_{1,2,3}}$ the reflection in the three symmetry planes containing the z axis.
These elements can be visualized from Fig. 4.

For the U sublattice of the hexagonal D^4_{6h} structure we first determine the 5f orbitals, $w_{i\mu}$, and then find the cell orbitals for contact, nearest-neighbor, and the next-nearest-neighbor pairs.

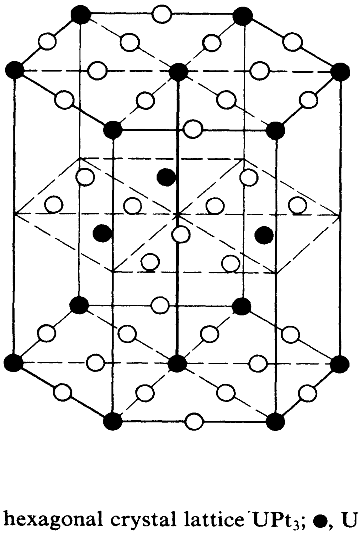

FIG. 2. The hexagonal crystal lattice UPt$_3$; ●, U atoms; ○, Pt atoms.

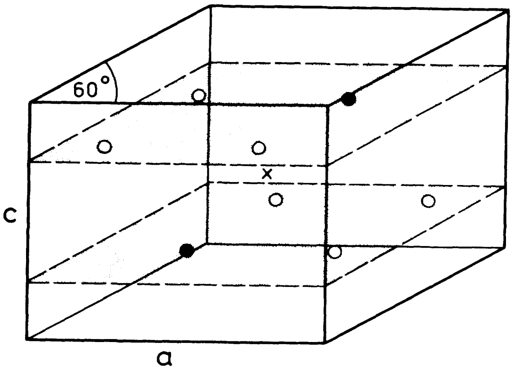

FIG. 3. The unit cell of UPt_3.

A. 5*f* orbitals

The one-electron orbitals, $w_{i\mu}(\mathbf{r},s)$, originate from the rotationally invariant free-atom states with total angular momentum $j=\frac{5}{2},\frac{7}{2}$. Of these fourteen states we ignore the eight $j=\frac{7}{2}$ states which are split from the six $j=\frac{5}{2}$ states by virtue of spin-orbit coupling. The splitting is clearly seen in the recent band-structure calculations of UPt_3. The $j=\frac{5}{2}$ states make the dominant $5f$ contribution to the Bloch states at the Fermi energy.[16–19] We look at these states as quasiparticle states. The quasiparticles are the f electrons. The f bands are moved to the vicinity of the Fermi energy and are narrowed by correlation effects.

By using the D_{3h} point symmetry of a U site, we project out of the $j=\frac{5}{2}$ states, $\psi_{5/2,m_j}$, the new basis states which transform according to the matrix representations of D_{3h}, Table I. By applying the projection operator method we get

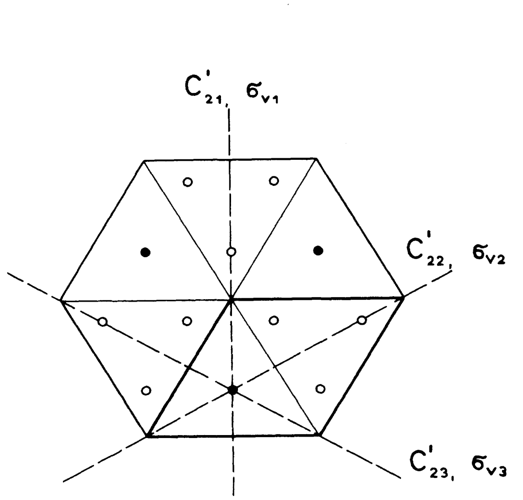

FIG. 4. Hexagonal plane; symmetry operations of the group D_{3h}, Eq. (4.1).

$$w_{7+}=\psi_{5/2,-5/2}=-\sqrt{6/7}\phi_{3,-3}\alpha+\sqrt{1/7}\phi_{3,-2}\beta\ , \tag{4.1}$$

$$w_{7-}=-\psi_{5/2,5/2}=\sqrt{1/7}\phi_{3,2}\alpha-\sqrt{6/7}\phi_{3,3}\beta\ , \tag{4.2}$$

$$w_{8+}=\psi_{5/2,1/2}=-\sqrt{3/7}\phi_{3,0}\alpha+\sqrt{4/7}\phi_{3,1}\beta\ , \tag{4.3}$$

$$w_{8-}=\psi_{5/2,-1/2}=-\sqrt{4/7}\phi_{3,-1}\alpha+\sqrt{3/7}\phi_{3,0}\beta\ , \tag{4.4}$$

$$w_{9+}=\psi_{5/2,-3/2}=-\sqrt{5/7}\phi_{3,-2}\alpha+\sqrt{2/7}\phi_{3,-1}\beta\ , \tag{4.5}$$

$$w_{9-}=\psi_{5/2,-3/2}=-\sqrt{2/7}\phi_{3,1}\alpha+\sqrt{5/7}\phi_{3,2}\beta\ , \tag{4.6}$$

where

$$\phi_{l,m}(\mathbf{r})=f_l(\mathbf{r})i^lY_{l,m}(\vartheta,\varphi) \tag{4.7}$$

and $\alpha=\delta_+(s)$, $\beta=\delta_-(s)$. The functions $f_l(\mathbf{r})$ have the full point symmetry. The orbitals $w_{i\mu}(\mu=+,-)$ transform under the symmetry operations of the group D_{3h} as

$$Rw_{i\mu}(\mathbf{r}-\mathbf{n}-\boldsymbol{\tau}_1,s)=\sum_{\mu'}w_{i\mu'}[\mathbf{r}-R(\mathbf{n}+\boldsymbol{\tau}_1),s]D^{(i)}_{\mu'\mu}(R)\ , \tag{4.8}$$

where the matrices $D^{(i)}_{\mu\mu'}$ are given in Table I.

We use the Condon-Shortley choice of the phases of the spherical harmonics Y_{lm}. The application of K gives

$$KY_{l,m}=Y^*_{l,m}=(-1)^{-m}Y_{l,-m}\ . \tag{4.9}$$

The phases of α and β are fixed by

$$K\alpha=\beta,\quad K\beta=-\alpha\ . \tag{4.10}$$

For the Kramers doublet we have

$$Kw_{i\mu}=\mu w_{i\,-\mu}(\mu=+,-);\quad \Gamma_i=\Gamma_7,\Gamma_8,\Gamma_9\ . \tag{4.11}$$

B. Cell contact pairs

The pair orbitals are composed of contact pairs at the two U sites of the unit cell. The contact-pair orbitals at each of the two sites are invariant under D_{3h}. The orbitals transform according to the irreducible representations Γ_{i_S} of S given by the decomposition of the direct product, $(\Gamma_7+\Gamma_8+\Gamma_9)\times(\Gamma_7+\Gamma_8+\Gamma_9)$ (cf. Table II),

$$\not{f}(\mathbf{r}s,\mathbf{r}'s';i_S\mu_S)=\sum_{\mu,\nu}C^{iji_S}_{\mu\nu\mu_S}A\not{f}(\mathbf{r}s,\mathbf{r}'s';i\mu,j\nu)\ , \tag{4.12}$$

where $\not{f}(\mathbf{r}s,\mathbf{r}'s';i\mu,j\nu)$ is the basic pair orbital at a U atom, $w_{i\mu}w_{j\nu}$. The coupling coefficients C are obtained by applying the projection operator,

$$P^{(i_S)}_{\mu_S\rho}=\frac{d}{n}\sum_R D^{(i_S)}_{\mu_S\rho}(R)^*R \tag{4.13}$$

to the product states,

$$\begin{aligned}P^{(i_S)}_{\mu_S\rho}w_{i\mu}w_{j\nu}&=\frac{d}{n}\sum_R D^{(i_S)}_{\mu_S\rho}(R)^*Rw_{i\mu}w_{j\nu}\\&=\frac{d}{n}\sum_R\sum_{\mu',\nu'}D^{(i_S)}_{\mu_S\rho}(R)^*D^{(i)}_{\mu'\mu}(R)D^{(j)}_{\nu'\nu}(R)w_{i\mu'}w_{jr'}\\&=\sum_{\mu',\nu}C^{iji_S}_{\mu'\nu'\mu_S}w_{i\mu'}w_{j\nu'}\ .\end{aligned} \tag{4.14}$$

TABLE I. The matrix representations of the point group D_{3h}; $D_{6h}=D_{3h}\times C_i$.

	E	$\bar{E}$	C_3^+	$\bar{C}_3^-$	C_3^-	$\bar{C}_3^+$
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1
Γ_3	1	1	1	1	1	1
Γ_4	1	1	1	1	1	1
Γ_5	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$	$\begin{pmatrix}\epsilon & 0\\0 & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon & 0\\0 & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$
Γ_6	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$	$\begin{pmatrix}\epsilon & 0\\0 & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon & 0\\0 & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$
Γ_7	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}-\epsilon & 0\\0 & -\epsilon^*\end{pmatrix}$	$\begin{pmatrix}-\epsilon^* & 0\\0 & -\epsilon\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$	$\begin{pmatrix}\epsilon & 0\\0 & \epsilon^*\end{pmatrix}$
Γ_8	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}-\epsilon & 0\\0 & -\epsilon^*\end{pmatrix}$	$\begin{pmatrix}-\epsilon^* & 0\\0 & -\epsilon\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & 0\\0 & \epsilon\end{pmatrix}$	$\begin{pmatrix}\epsilon & 0\\0 & \epsilon^*\end{pmatrix}$
Γ_9	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}-1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$

	σ_{v_1}	σ_{v_2}	σ_{v_3}	$\bar{\sigma}_{V_1}$	$\bar{\sigma}_{v_2}$	σ_{v_3}
Γ_1	1	1	1	1	1	1
Γ_2	-1	-1	-1	-1	-1	-1
Γ_3	1	1	1	1	1	1
Γ_4	-1	-1	-1	-1	-1	-1
Γ_5	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & \epsilon\\\epsilon^* & 0\end{pmatrix}$	$\begin{pmatrix}0 & \epsilon^*\\\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & \epsilon\\\epsilon^* & 0\end{pmatrix}$	$\begin{pmatrix}0 & \epsilon^*\\\epsilon & 0\end{pmatrix}$
Γ_6	$\begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & -\epsilon\\-\epsilon^* & 0\end{pmatrix}$	$\begin{pmatrix}0 & -\epsilon^*\\-\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & -1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & -\epsilon\\-\epsilon^* & 0\end{pmatrix}$	$\begin{pmatrix}0 & -\epsilon^*\\-\epsilon & 0\end{pmatrix}$
Γ_7	$\begin{pmatrix}0 & -i\\-i & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\epsilon^*\\-i\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\epsilon\\i\epsilon^* & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\\i & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\epsilon^*\\i\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\epsilon\\-i\epsilon^* & 0\end{pmatrix}$
Γ_8	$\begin{pmatrix}0 & i\\i & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\epsilon^*\\i\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\epsilon\\-i\epsilon^* & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\\-i & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\epsilon^*\\-i\epsilon & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\epsilon\\i\epsilon^* & 0\end{pmatrix}$
Γ_9	$\begin{pmatrix}0 & i\\i & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\\i & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\\-i & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\\-i & 0\end{pmatrix}$	$\begin{pmatrix}0 & -i\\-i & 0\end{pmatrix}$	$\begin{pmatrix}0 & i\\i & 0\end{pmatrix}$

Here n is the number of group elements and d the dimension of Γ_{i_S}. The coefficients C, defined by comparing Eq. (4.12) with Eq. (4.14), are given in Table III. We note that in the case of contact pairs, where the two mates are at one and the same site, $\mathcal{S}=S$, Eq. (3.11).

To get the cell pairs which exhibit the complete symmetry of $G=D_{6h}$, we take into account the group T. The elements of T send the contact pair at one site either into itself or into the pair at the other site,

TABLE I. (*Continued*).

	σ_h	$\bar{\sigma}_h$	S_3^+	$\bar{S}_3^-$	S_3^-	$\bar{S}_3^+$
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1
Γ_3	-1	-1	-1	-1	-1	-1
Γ_4	-1	-1	-1	-1	-1	-1
Γ_5	$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$	$\begin{bmatrix}\epsilon^* & 0\\ 0 & \epsilon\end{bmatrix}$	$\begin{bmatrix}\epsilon & 0\\ 0 & \epsilon^*\end{bmatrix}$	$\begin{bmatrix}\epsilon & 0\\ 0 & \epsilon^*\end{bmatrix}$	$\begin{bmatrix}\epsilon^* & 0\\ 0 & \epsilon\end{bmatrix}$
Γ_6	$\begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}-\epsilon^* & 0\\ 0 & -\epsilon\end{bmatrix}$	$\begin{bmatrix}-\epsilon & 0\\ 0 & -\epsilon^*\end{bmatrix}$	$\begin{bmatrix}-\epsilon & 0\\ 0 & -\epsilon^*\end{bmatrix}$	$\begin{bmatrix}-\epsilon^* & 0\\ 0 & -\epsilon\end{bmatrix}$
Γ_7	$\begin{bmatrix}-i & 0\\ 0 & i\end{bmatrix}$	$\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}$	$\begin{bmatrix}i\epsilon & 0\\ 0 & -i\epsilon^*\end{bmatrix}$	$\begin{bmatrix}-i\epsilon^* & 0\\ 0 & i\epsilon\end{bmatrix}$	$\begin{bmatrix}i\epsilon^* & 0\\ 0 & -i\epsilon\end{bmatrix}$	$\begin{bmatrix}-i\epsilon & 0\\ 0 & i\epsilon^*\end{bmatrix}$
Γ_8	$\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}$	$\begin{bmatrix}-i & 0\\ 0 & i\end{bmatrix}$	$\begin{bmatrix}-i\epsilon & 0\\ 0 & i\epsilon^*\end{bmatrix}$	$\begin{bmatrix}i\epsilon^* & 0\\ 0 & -i\epsilon\end{bmatrix}$	$\begin{bmatrix}-i\epsilon^* & 0\\ 0 & i\epsilon\end{bmatrix}$	$\begin{bmatrix}i\epsilon & 0\\ 0 & -i\epsilon^*\end{bmatrix}$
Γ_9	$\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}$	$\begin{bmatrix}-i & 0\\ 0 & i\end{bmatrix}$	$\begin{bmatrix}-i & 0\\ 0 & i\end{bmatrix}$	$\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}$	$\begin{bmatrix}-i & 0\\ 0 & i\end{bmatrix}$	$\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}$

	C'_{21}	C'_{22}	C'_{23}	$\bar{C}'_{21}$	$\bar{C}'_{22}$	$\bar{C}'_{23}$
Γ_1	1	1	1	1	1	1
Γ_2	-1	-1	-1	-1	-1	-1
Γ_3	-1	-1	-1	-1	-1	-1
Γ_4	1	1	1	1	1	1
Γ_5	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon\\ \epsilon^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon^*\\ \epsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon\\ \epsilon^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon^*\\ \epsilon & 0\end{bmatrix}$
Γ_6	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon\\ \epsilon^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon^*\\ \epsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon\\ \epsilon^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon^*\\ \epsilon & 0\end{bmatrix}$
Γ_7	$\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon^*\\ -\epsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon\\ -\epsilon^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\epsilon^*\\ \epsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\epsilon\\ \epsilon^* & 0\end{bmatrix}$
Γ_8	$\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon^*\\ -\epsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & \epsilon\\ -\epsilon^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\epsilon^*\\ \epsilon & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\epsilon\\ \epsilon^* & 0\end{bmatrix}$
Γ_9	$\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$

$$T_1 = \{E,0\}, \quad T_2 = \{J,\tau\} \ . \tag{4.15}$$

Here, $\{J,\tau\}$ is the inversion at $\tau_1 = -\tau/2$ followed by τ, Fig. 1. The group T is ismorphic to the point group C_i (elements E and J). The irreducible representations of C_i are Γ_1^+ and Γ_1^-. For the group G, the representations are then given by direct products: $\Gamma_{i_{6h}} = \Gamma_{i_{3h}} \times \Gamma_1^{\pm} \equiv \Gamma_{i_{3h}}^{\pm}$.

The contact orbitals at the two atomic sites are

$$\mathscr{f}(\kappa,i_{3h}\mu_{3h})=\mathscr{f}\left[\mathbf{r}+\frac{\tau}{2},s\,;\tau'+\frac{\tau}{2},s';i_{3h}\mu_{3h}\right],\quad \kappa=1$$

$$=\mathscr{f}\left[\mathbf{r}-\frac{\tau}{2},s\,;\mathbf{r}'-\frac{\tau}{2},s';i_{3h}\mu_{3h}\right],\quad \kappa=2\ . \tag{4.16}$$

The cell pair orbitals are

$$\mathscr{f}(i_{6h}\mu_{6h})=\sum_{\kappa=1,2}C(i_{3h},i_{6h};\kappa)\mathscr{f}(\kappa)\ , \tag{4.17}$$

TABLE II. Multiplication table for the representations Γ_7, Γ_8, Γ_9 of D_{3h}.

	Γ_7	Γ_8	Γ_9
Γ_7	$\Gamma_1+\Gamma_2+\Gamma_6$	$\Gamma_3+\Gamma_4+\Gamma_5$	$\Gamma_5+\Gamma_6$
Γ_8		$\Gamma_1+\Gamma_2+\Gamma_6$	$\Gamma_5+\Gamma_6$
Γ_9			$\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$

where the coefficients $C(i_{3h},i_{6h};\kappa)$ are given in Table IV. By using Eqs. (4.12)–(4.17) and Tables III and IV we write the cell orbitals as

$$\mathscr{f}(i_{6h}\mu_{6h})=\frac{e^{i\delta}}{2}\left\{\left[w_{i\mu}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{j\nu}\left[\mathbf{r}'+\frac{\tau}{2},s'\right]-w_{j\nu}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{i\mu}\left[\mathbf{r}'+\frac{\tau}{2},s'\right]\right]\right.$$
$$\left.\pm\left[w_{i\mu}\left[\mathbf{r}-\frac{\tau}{2},s\right]w_{j\nu}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]-w_{j\nu}\left[\mathbf{r}-\frac{\tau}{2},s\right]w_{i\mu}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]\right]\right\}\ . \tag{4.18}$$

Here, $i_{6h}=i_{3h}^{\pm}(i,j)$, and $i_{3h}=\Gamma_1$, Γ_2, Γ_5, and Γ_6. The phase factors $e^{i\delta}$ are given in Table V together with the relations between the representations of the pair orbitals i_{3h} and the representations of the single-electron orbitals i and j.

Because of the antisymmetry which is evident from Eq. (4.18), the pair orbitals which are transforming according to the i_{3h} representations Γ_2, $\Gamma_{6(7,7)}$, $\Gamma_{6(8,8)}$, $\Gamma_{3(9,9)}$, and $\Gamma_{4(9,9)}$ vanish. The pair orbitals which transform according to the one-dimensional representations $\Gamma_3^{\pm}$ and $\Gamma_4^{\pm}$ of D_{6h} are given by

$$\mathscr{f}(\Gamma_{3,4}^{\pm})=\frac{1\pm\{J,\tau\}}{\sqrt{2}}$$
$$\times\frac{A}{\sqrt{2}}\left[w_{7+}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{8-}\left[\mathbf{r}'+\frac{\tau}{2},s'\right]\right.$$
$$\left.\pm w_{7-}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{8+}\left[\mathbf{r}'+\frac{\tau}{2},s'\right]\right]\ . \tag{4.19}$$

TABLE III. The coupling coefficients $C_{\mu\nu\mu_S}^{iji_S}$ of Eq. (4.11). The basis index μ_S is omitted for the one-dimensional representations of S.

i_S,μ_S	Γ_1	Γ_2	$\Gamma_6,+$	$\Gamma_6,-$	i_S,μ_S	Γ_1	Γ_2	$\Gamma_6,+$	$\Gamma_6,-$
7+ 7+	0	0	1	0	8+ 8+	0	0	1	0
7+ 7−	$1/\sqrt{2}$	$1/\sqrt{2}$	0	0	8+ 8−	$1/\sqrt{2}$	$1/\sqrt{2}$	0	0
7− 7+	$-1/\sqrt{2}$	$1/\sqrt{2}$	0	0	8− 8+	$-1/\sqrt{2}$	$1/\sqrt{2}$	0	0
7−7 −	0	0	0	1	8−8 −	0	0	0	1
i_S,μ_S	Γ_1	Γ_2	Γ_3	Γ_4	i_S,μ_S	Γ_3	Γ_4	$\Gamma_5,+$	$\Gamma_5,-$
9+ 9+	0	0	$1/\sqrt{2}$	$1/\sqrt{2}$	7+ 8+	0	0	1	0
9+ 9−	$1/\sqrt{2}$	$1/\sqrt{2}$	0	0	7+ 8−	$1/\sqrt{2}$	$1/\sqrt{2}$	0	0
9− 9+	$-1/\sqrt{2}$	$1/\sqrt{2}$	0	0	7− 8+	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	0
9− 9−	0	0	$-1/\sqrt{2}$	1/2	7− 8−	0	0	0	1
i_S,μ_S	$\Gamma_5,+$	$\Gamma_5,-$	$\Gamma_6,+$	$\Gamma_6,-$	i_S,μ_S	$\Gamma_5,+$	$\Gamma_5,-$	$\Gamma_6,+$	$\Gamma_6,-$
7+ 9+	0	1	0	0	8+ 9+	0	0	0	1
7+ 9−	0	0	0	−1	8+ 9−	0	−1	0	0
7− 9+	0	0	1	0	8− 9+	1	0	0	0
7− 9−	1	0	0	0	8− 9−	0	0	1	0

TABLE IV. The coefficients $C(i_{3h},i_{6h};\kappa)$ of Eq. (4.17) for the contact cell orbitals; $i_{6h}=i_{3h}^{\pm}$.

i_G κ	i_{3h}^{+}	i_{3h}^{-}
1	$1/\sqrt{2}$	$1/\sqrt{2}$
2	$1/\sqrt{2}$	$-1/\sqrt{2}$

Here, + in the bracket refers to $\Gamma_3^{\pm}$ whereas − refers to $\Gamma_4^{\pm}$.

The time-reversal symmetric orbitals are given by

$$K\not{f}(i_{6h}\mu)=\sum_{\mu'}\not{f}(i_{6h}\mu')D_{\mu'\mu}^{(i_{6h})}(-i\sigma_y)\ , \tag{4.20}$$

where

$$D_{\mu'\mu}^{(6h)}\equiv D_{\mu'\mu}^{(3h^{\pm})}=\begin{cases}1, & \Gamma_{i_{3h}}=\Gamma_1,\Gamma_4\\ -1, & \Gamma_3,\Gamma_2\\ \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}, & \Gamma_5,\Gamma_6\ .\end{cases} \tag{4.21}$$

C. Nearest-neighbor cell pairs

A given U atom has six nearest-neighbor atoms. Three atoms lie in the plane above and three lie in the plane below that containing the U atom. The six equivalent atom pairs, 0-1, . . . , 0—6, are shown in Fig. 5. The symmetry operations which send a given pair, 0-1, into itself and the other pairs are given by the group $T=C_{3h}=\{E,C_3^+,C_3^-,\sigma_h,S_3^+,S_3^-\}$. We proceed to construct the cell orbitals arising from two electrons at the nearest-neighbor U sites.

First, we find the pair orbitals at a *given atom pair*, 0-1. The two atoms are separated by the nonprimitive translation, $|\tau|=4.15$ Å. The symmetry operations which leave both of the two atoms invariant form the group $S=C_s'=\{E,\sigma_{v_2}\}$ which is isomorphic to C_s, Table VI. The one-electron orbitals compatible with the symmetry of C_s' transform according to the one-dimensional representations Γ_3 and Γ_4 of C_s'. The compatibility relations between the representations of D_{3h} and C_s' are evident from the Tables I and VI. Furthermore, the pair orbitals transform according to the one-dimensional representations Γ_1 and Γ_2 of C_s', as is seen from Table VI.

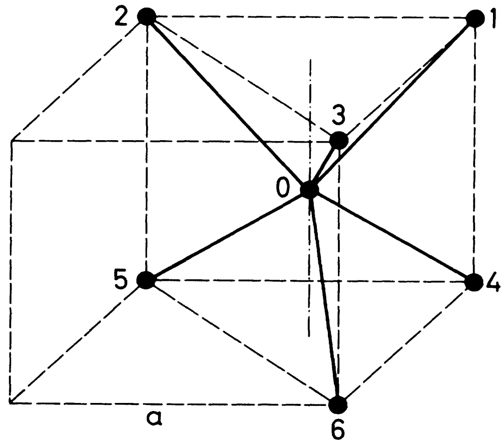

FIG. 5. The six nearest-neighbor U atoms.

TABLE V. The connection between the pair of one-electron orbitals, $i\mu$ and $j\nu$, and the pair orbital $i_{3h}\mu_{3h}$. The phase factor of Eq. (4.18).

$i\mu$	$j\nu$	i_{3h}	μ_{3h}	$e^{i\delta}$
7+	7−	1		1
8+	8−	1		1
9+	9−	1		1
7+	8+	5	+	1
7−	8−	5	−	1
7−	9−	5	+	1
7+	9+	5	−	1
7−	9+	6	+	1
7+	9−	6	−	−1
8−	9+	5	+	1
8+	9−	5	−	−1
8−	9−	6	+	1
8+	9+	6	−	1

The basic product set, $w_{i\mu}w_{j\nu}$, forms a four-dimensional vector space ($\mu,\nu=\pm$). Hence, the two one-dimensional representations Γ_1 and Γ_2 each occur twice. We introduce the degeneracy indices a and b; $i_S=\Gamma_1^a$, Γ_1^b, Γ_2^a, and Γ_2^b. Applying the projection operator $P^{(i_S)}$ to the product set, we get the pair orbitals in the form

$$\not{f}(\mathbf{r}s,\mathbf{r}'s';i_S)=\sum_{\mu,\nu}C_{\mu\nu}^{iji_S}A\left[w_{i\mu}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{j\nu}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]\right]\ . \tag{4.22}$$

The coupling coefficients C are evaluated in Appendix A; the result is given in Table VII.

In addition to the symmetry elements C_s' there exists the inversion center between the two U atoms. Hence, the

TABLE VI. The double group C_s: Character table and multiplication table.

C_s	E	$\bar{E}$	σ_h	$\bar{\sigma}_h$
Γ_1	1	1	1	1
Γ_2	1	1	−1	1
Γ_3	1	−1	i	$-i$
Γ_4	1	−1	$-i$	i

	Γ_3	Γ_4
Γ_3	Γ_2	Γ_1
Γ_4	Γ_1	Γ_2

TABLE VII. The coefficients $C_{\mu\nu}^{iji_S}$ of Eq. (4.22); a and b label the degeneracy of the representations of S. The common factor $1/\sqrt{2}$ is omitted.

i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b	i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b
7+ 7+	0	$i\epsilon^*$	0	$i\epsilon^*$	8+ 8+	0	$i\epsilon^*$	0	$i\epsilon^*$
7+ 7−	1	0	1	0	8+ 8−	1	0	1	0
7− 7+	−1	0	1	0	8− 8+	−1	0	1	0
7− 7−	0	$-i\epsilon$	0	$i\epsilon$	8− 8+	0	$-i\epsilon$	0	$i\epsilon$
i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b	i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b
9+ 9+	0	i	0	i	7+ 8+	ϵ^*	0	ϵ^*	0
9+ 9−	1	0	1	0	7+ 8−	0	i	0	i
9− 9+	−1	0	1	0	7− 8+	0	$-i$	0	i
9− 9−	0	$-i$	0	i	7− 8−	ϵ	0	$-\epsilon$	0
i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b	i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b
7+ 9+	ϵ	0	0	$i\epsilon$	8+ 9+	0	$i\epsilon$	0	$i\epsilon$
7+ 9−	0	$i\epsilon$	ϵ	0	8+ 9−	ϵ	0	ϵ	0
7− 9+	0	$i\epsilon$	$-\epsilon$	0	8− 9+	$-\epsilon$	0	ϵ	0
7− 9−	ϵ^*	0	0	$-i\epsilon^*$	8− 9−	0	$-i\epsilon^*$	0	$i\epsilon^*$

basic set of antisymmetrized pair orbitals at 0-1 has the form,

$$f(\kappa,i_S)=\{E,0\}f(i_S),\quad \kappa=1$$

$$=\{J,\tau\}f(i_S),\quad \kappa=2\ . \tag{4.23}$$

The pair orbitals of even and odd parity, transforming according to the representations $i_{\mathscr{S}}=i_S^{\pm}$ of the group $\mathscr{S}=C_s'C_i$, are given by

$$f(i_{\mathscr{S}})=\sum_{\kappa=1,2,} C(i_{\mathscr{S}},i_S;\kappa)f(\kappa,i_S)\ . \tag{4.24}$$

Here, the C's are given by Table IV, when $i_{\mathscr{S}}$ is substituted for $i_{3h}^{\pm}$. We insert Eq. (4.23) into (4.24) and get

$$f(\mathbf{r}s,\mathbf{r}'s';i_{\mathscr{S}})=\sum_{\mu,\nu} C_{\mu\nu}^{iji_S}\frac{1}{[2(1+\delta_{ij})]^{1/2}}$$
$$\times\left\{\left[w_{i\mu}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{j\nu}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]-w_{j\nu}\left[\mathbf{r}-\frac{\tau}{2},s\right]w_{i\mu}\left[\mathbf{r}'+\frac{\tau}{2},s'\right]\right]\right.$$
$$\left.\pm\left[w_{i\mu}\left[\mathbf{r}-\frac{\tau}{2},s\right]w_{j\nu}\left[\mathbf{r}'+\frac{\tau}{2},s\right]-w_{j\nu}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{i\mu}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]\right]\right\}\ . \tag{4.25}$$

This equation is the final form of the pair orbitals at a given pair of U sites. For $i=j$, the orbitals transforming according to Γ_1^b, Γ_2^a, and Γ_2^b have odd parity and the orbitals Γ_1^a has even parity.

Finally, the cell orbitals are found to be the proper linear combinations of the pair orbitals at the six equivalent atom pairs, 0-1 to 0-6 (Fig. 5). By applying the elements of $T=C_{3h}$ to a given pair orbital f we generate the six linearly independent orbitals:

$$f_1=Ef,\quad f_2=C_3^+f,\quad f_3=C_3^-f\ ,$$

$$f_4=\sigma_h f,\quad f_5=S_3^+f,\quad f_6=S_3^-f\ . \tag{4.26}$$

To find the linear combinations of the f_λ's which transform according to the irreducible representations of $D_{6h}=C_{3h}\mathscr{S}$, we apply the projection operator method; the result is

$$f(\mathbf{r}s,\mathbf{r}'s';i_{6h}\mu_{6h})=\sum_{\lambda=1}^{6} C(i_{\mathscr{S}},i_{6h}\mu_{6h};\lambda)f_\lambda(i_{\mathscr{S}})\ . \tag{4.27}$$

The coupling constants C are derived in Appendix B, up to a phase factor that we are free to choose in order to fulfill the time-reversal symmetry, Eq. (4.20). The C's are given in Table VIII.

TABLE VIII. The coefficients $C(i_{\mathscr{S}},i_{6h}\mu_{6h};\lambda)$ of Eq. (4.27) for the nearest-neighbor cell orbitals. The factor $1/\sqrt{6}$ is omitted; $\epsilon=\exp(2\pi i/3)$. The C's are labeled by the representations of D_{3h}; $i_{6h}=i_{3h}^{\pm}$.

Case (a): $i_{\mathscr{S}}=\Gamma_1^+,\Gamma_1^-$

i_{3h},μ_{3h}	Γ_1	Γ_3	$\Gamma_5,+$	$\Gamma_5,-$	$\Gamma_6,+$	$\Gamma_6,-$
$\lambda=1$	1	i	ϵ	ϵ^*	$i\epsilon$	$-i\epsilon^*$
$\lambda=2$	1	i	ϵ^*	ϵ	$i\epsilon^*$	$-i\epsilon$
$\lambda=3$	1	i	1	1	i	$-i$
$\lambda=4$	1	$-i$	ϵ	ϵ^*	$-i\epsilon$	$i\epsilon^*$
$\lambda=5$	1	$-i$	ϵ^*	ϵ	$-i\epsilon^*$	$i\epsilon$
$\lambda=6$	1	$-i$	1	1	$-i$	i

Case (b): $i_{\mathscr{S}}=\Gamma_2^+,\Gamma_2^-$

i_{3h},μ_{3h}	Γ_2	Γ_4	$\Gamma_5,+$	$\Gamma_5,-$	$\Gamma_6,+$	$\Gamma_6,-$
$\lambda=1$	1	i	ϵ	$-\epsilon^*$	$i\epsilon$	$i\epsilon^*$
$\lambda=2$	1	i	ϵ^*	$-\epsilon$	$i\epsilon^*$	$i\epsilon$
$\lambda=3$	1	i	1	-1	i	i
$\lambda=4$	1	$-i$	ϵ	$-\epsilon^*$	$-i\epsilon$	$-i\epsilon^*$
$\lambda=5$	1	$-i$	ϵ^*	$-\epsilon$	$-i\epsilon^*$	$-i\epsilon$
$\lambda=6$	1	$-i$	1	-1	$-i$	$-i$

D. Next-nearest-neighbor cell pairs

Each U atom has six next-nearest-neighbor (NNN) atoms in the plane perpendicular to the z axis (Fig. 6). The two atoms of a pair are separated by a primitive translation **n**. The two basis vectors are given by $\tau_1=\tau_2=-\tau/2$. The symmetry operators that leave both of the two atoms invariant lead to the point group $C_s=\{E,\sigma_h\}=S$, Table IV. The antisymmetrized pair orbitals invariant under S are given by

$$\mathscr{F}(\mathbf{r}s,\mathbf{r}'s';i_S)=\sum_{\mu,\nu}C_{\mu\nu}^{iji_S}A\left[w_{i\mu}\left[\mathbf{r}+\frac{\tau}{2},s\right]\times w_{j\nu}\left[\mathbf{r}'+\frac{\tau}{2}-\mathbf{n},s'\right]\right]. \quad (4.28)$$

The coupling coefficients are found in Table IX. The time-reversal behavior is $K\mathscr{F}(\Gamma_1)=\mathscr{F}(\Gamma_1)$ and $K\mathscr{F}(\Gamma_2)=-\mathscr{F}(\Gamma_2)$. In addition to the elements of C_s, the pair of atoms is left invariant by the group $C_s'=\{E,\sigma_{v_1}\}$. The reflection on the plane parallel to the z axis, σ_{v_1}, sends the pair 0-1 into 0-1′, cf. Fig. 6. The latter pair is transformed into the former by a primitive translation and the result is an interchange of the atoms 0 and 1. Hence, the pair orbital at 0-1 is invariant under the group that is isomorphic to $C_{3v}=\{E,\sigma_h,\sigma_{v_1},C_{21}'\}$. This group $(=\mathscr{S})$ is the direct product, $C_s\times C_s'$; the characters are found in Table X. The pair orbital transforms according to an irreducible representation of $\mathscr{S}$,

$$\mathscr{F}(i_{\mathscr{S}})=\sum_{\kappa=1,2}C(i_S;i_{\mathscr{S}},\kappa)\mathscr{F}(\kappa)\ . \quad (4.29)$$

Here $\mathscr{F}(1)=E\mathscr{F}(i_S)$ and $\mathscr{F}(2)=\sigma_{v_1}\mathscr{F}(i_S)$; $i_S=i_S(i,j)$. The coupling coefficients are given in Table XI. The corresponding time-reversal behavior is

$$K\mathscr{F}(\Gamma_i)=\mathscr{F}(\Gamma_i),\quad i=1,4$$
$$=-\mathscr{F}(\Gamma_i),\quad i=2,3\ . \quad (4.30)$$

For $i=j$, the following representations of $\mathscr{S}$ do not occur: $i_{\mathscr{S}}=\Gamma_2(\Gamma_2^a,\Gamma_2^b)$, $\Gamma_1(\Gamma_1^a)$, and $\Gamma_3(\Gamma_1^a)$. Equation (4.29) presents the final form of the NNN pair orbitals for a given pair of U atoms.

There are six equivalent pairs that enter a cell orbital. Three of these pairs lie in the plane of the center atom 0, Fig. 7: 0-1, 0-2, and 0-3. The other three equivalent pairs lie in the parallel plane through the other atom of the unit cell: 0′-4, 0′-5, and 0′-6.

The three pair orbitals in the plane of atom 0 are generated by the symmetry elements of C_3; we have $\mathscr{F}_1=E\mathscr{F}(i_{\mathscr{S}})$, $\mathscr{F}_2=C_3^+\mathscr{F}(i_{\mathscr{S}})$, and $\mathscr{F}_3=C_3^-\mathscr{F}(i_{\mathscr{S}})$. Using the projection operator method, we find the proper linear combinations which transform according to the irreducible representations of D_{3h},

$$\mathscr{F}(\mathbf{r}s,\mathbf{r}'s';i_{3h}\mu_{3h})=\sum_{\lambda}C(i_{\mathscr{S}};i_{3h}\mu_{3h},\lambda)\mathscr{F}_\lambda(i_{\mathscr{S}})\ . \quad (4.31)$$

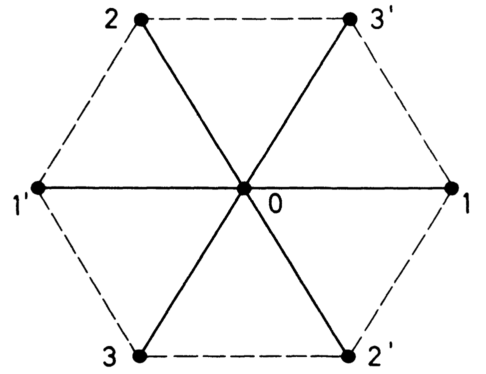

FIG. 6. The six next-nearest-neighbor U atoms.

TABLE IX. The coefficients $C_{\mu\nu}^{iji_S}$ of Eq. (4.28); see also Table VII.

i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b	i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b
$7+7+$	0	0	i	1	$8+8+$	0	0	i	1
$7+7-$	1	i	0	0	$8+8-$	1	i	0	0
$7-7+$	-1	i	0	0	$8-8+$	-1	i	0	0
$7-7-$	0	0	i	-1	$8-8-$	0	0	i	-1
i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b	i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b
$9+9+$	0	0	i	$+1$	$7+8+$	1	i	0	0
$9+9-$	1	i	0	0	$7+8-$	0	0	1	i
$9-9+$	-1	i	0	0	$7-8+$	0	0	1	$-i$
$9-9-$	0	0	$+i$	-1	$7-8-$	1	$-i$	0	0
i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b	i_S	Γ_1^a	Γ_1^b	Γ_2^a	Γ_2^b
$7+9+$	1	i	0	0	$8+9+$	0	0	i	1
$7+9-$	0	0	1	i	$8+9-$	1	i	0	0
$7-9+$	0	0	1	$-i$	$8-9+$	-1	i	0	0
$8-9-$	1	$-i$	0	0	$8-9-$	0	0	i	-1

The coupling constants are listed in Table XII. The final step in constructing the cell pair orbitals at the NNN atoms consists in applying the symmetry operations $T_{1,2}$, Eq. (4.15), to $\mathscr{f}(i_{3h},\mu_{3h})$.

V. T_c EQUATION

At this point we employ the Cooper pairs of Sec. III in order to symmetrize the vertex equation for the basic pair eigenfunctions, Eq. (2.9). Using the transformation (3.17) that relates the basic pairs to the cell pairs, the vertex equation becomes

$$g(d,i_\gamma\mu)=-\frac{1}{\beta_c}\sum_{\omega}\sum_{d'}\sum_{i',\gamma',\mu'}g(d',i'_{\gamma'}\mu')\times\langle d',i'_{\gamma'}\mu'\,|\,\mathscr{K}\,|\,d,i_\gamma\mu\rangle\ . \tag{5.1}$$

Here $i_\gamma\equiv\{i_G,\gamma\}$, where γ is a degeneracy index $(1,2,\dots)$ that labels the cell pairs corresponding to the same representation $i_G;\mu=\mu_G$. The kernel $\mathscr{K}$ is invariant under the symmetry operations R_λ; hence, we have

$$\langle d',i'_{\gamma'}\mu'\,|\,\mathscr{K}\,|\,d,i_\gamma\mu\rangle=\langle d',i_{\gamma'}\mu\,|\,\mathscr{K}\,|\,d,i_\gamma\mu\rangle\delta_{ii'}\delta_{\mu\mu'}\ . \tag{5.2}$$

This equation follows directly from the orthogonality theorem,

$$\sum_\lambda D^{(i)}_{\mu'''\mu''}(R_\lambda)^*D^{(i')}_{\mu'\mu}(R_\lambda)=0 \quad \text{for}\quad i\neq i',\ \mu'''\neq\mu',\ \mu''\neq\mu\ . \tag{5.3}$$

In summary $\mathscr{K}$ only connects cell orbitals of one and the same representation, i_G, and of the same basis vector, μ_G. Thus, the eigenfunctions obey the sets of equations,

$$g(d,i_\gamma\mu)=-\frac{1}{\beta_c}\sum_{\omega'}\sum_{d',\gamma'}g(d',i_{\gamma'}\mu)\times\langle d',i_{\gamma'}\mu\,|\,\mathscr{K}\,|\,d,i_\gamma\mu\rangle\ . \tag{5.4}$$

Each set in general leads to a different $T_c(i_G)$. For a degenerate representation i_G, the matrix elements of $\mathscr{K}$ have the same value for the different basis vectors, $\mu\equiv\mu_G$. In evaluating $T_c(i_G)$, we may choose any μ_G. For $T<T_c$, the degeneracy is lifted when the GL free energy is minimized to yield the equilibrium state, as shown by other authors.[4-6] As for T_c, which representation i_G yields the highest transition temperature will depend on the pairing interaction I of the kernel $\mathscr{K}$,

$$\langle d',i_{\gamma'}\mu\,|\,\mathscr{K}\,|\,d,i_\gamma\mu\rangle=\sum_{d'',\gamma''}\langle d',i_{\gamma'}\mu\,|\,G(\omega)G(-\omega)\,|\,d'',i_{\gamma''}\mu\rangle\times\langle d'',i_{\gamma''}\mu\,|\,I(\omega-\omega')\,|\,d,i_\gamma\mu\rangle\ , \tag{5.5}$$

where GG and I have the same symmetry properties as $\mathscr{K}$. The anomalous Green's function is given by

TABLE X. Character table of the point group C_{3v}.

	E	σ_h	σ_{v_1}	C'_{21}
Γ_1	1	1	1	1
Γ_2	1	-1	1	-1
Γ_3	1	1	-1	-1
Γ_4	1	-1	-1	1

TABLE XI. The coefficients $C(i_s=\Gamma_1,i_{\mathscr{S}};\kappa)$ of Eq. (4.29). For $i_S=\Gamma_2$, the coefficients remain unchanged when Γ_1,Γ_3 ($=i_{\mathscr{S}}$) are replaced by Γ_2,Γ_4, respectively.

κ	$i_{\mathscr{S}}=\Gamma_1$	Γ_2
1	$1/\sqrt{2}$	$i/\sqrt{2}$
2	$1/\sqrt{2}$	$-i/\sqrt{2}$

TABLE XII. The coefficients $C(i_{\mathscr{S}},i_{3h}\mu_{3h};\lambda)$ of Eq. (4.31) for the next-nearest-neighbor cell orbitals. The common factor $1/\sqrt{2}$ is omitted.

	$i_{\mathscr{S}}=\Gamma_1$				$i_{\mathscr{S}}=\Gamma_2$		
i_{3h},μ_{3h}	Γ_1	$\Gamma_5,+$	$\Gamma_5,-$	i_{3h},μ_{3h}	Γ_3	$\Gamma_6,+$	$\Gamma_6,-$
$\lambda=1$	1	1	1	$\lambda=1$	1	1	-1
$\lambda=2$	1	ϵ	ϵ^*	$\lambda=2$	1	ϵ	$-\epsilon^*$
$\lambda=3$	1	ϵ^*	ϵ	$\lambda=3$	1	ϵ^*	$-\epsilon$
	$i_{\mathscr{S}}=\Gamma_3$				$i_{\mathscr{S}}=\Gamma_4$		
i_{3h},μ_{3h}	Γ_2	$\Gamma_5,+$	$\Gamma_5,-$	i_{3h},μ_{3h}	Γ_4	$\Gamma_6,+$	$\Gamma_6,-$
$\lambda=1$	1	1	-1	$\lambda=1$	1	1	1
$\lambda=2$	1	ϵ	$-\epsilon^*$	$\lambda=2$	1	ϵ	ϵ^*
$\lambda=3$	1	ϵ^*	$-\epsilon$	$\lambda=3$	1	ϵ^*	ϵ

$$\langle d,i_\gamma\mu\,|\,G(\omega)G(-\omega)\,|\,d',i_{\gamma'}\mu\rangle=\frac{1}{N_0}\sum_{\mathbf{k},\rho,\rho'}F^*(d,i_\gamma\mu)\frac{1}{[\omega-\epsilon_\rho(\mathbf{k})][-\omega-\epsilon_{\rho'}(-\mathbf{k})]}F(d',i_{\gamma'}\mu) \tag{5.6}$$

where N_0 = number of unit cells; F also depends on $\mathbf{k},\rho,\rho'$ and is given by

$$F(\mathbf{k},\rho\rho';d,i_\gamma\mu)=\sum_{\mu_i,\mu_2}\sum_{\lambda,\kappa}C^{i_1i_2i_\gamma}_{\mu_1\mu_2\mu}e^{i\mathbf{k}\cdot\mathbf{d}}a^*_{i_1\mu_1,\tau_1}(\mathbf{k}\rho)a^*_{i_2\mu_2,\tau_2}(-\mathbf{k}'_\rho)\ . \tag{5.7}$$

Here $\mathbf{d}=\{d,\lambda,\kappa\}$ and $\tau_{1,2}=\tau_{1,2}(\kappa)$; C depends on the angular direction λ and on the parameter κ that interchanges the two sites, cf. Eq. (3.12). This equation for the function F is derived in the Appendix C. There, one also finds the pairing interaction I of Eq. (5.5) expressed in terms of the interaction between basic pairs: Eq. (C6).

The central equation for the set of eigenfunctions of i_G, Eq. (5.4), reduces to a simple form for special cases of $\mathscr{K}$. Such a case is the *contact model.* Here, the two mates of a pair are at one and the same atomic site before the scattering event takes place. After the event, the two mates are again at *one* site; it may or may not be different from the initial site. This model is adopted in Ref. 1 to discuss T_c of BCS superconductors. In the mean time, it has been applied successfully to several d-band superconductors.[8]

For even- and odd-parity superconductors the contact kernel ($d=d'=0$) is

$$\langle i_\gamma\mu\,|\,\mathscr{K}\,|\,i_{\gamma'}\mu\rangle=\frac{1}{N_0}\sum_{\mathbf{k},\rho,\rho';\gamma''}F^*(i_\gamma\mu)\frac{1}{[\omega-\epsilon_\rho(\mathbf{k})][-\omega-\epsilon_{\rho'}(-\mathbf{k})]}F(i_{\gamma''}\mu)\langle i_{\gamma''}\mu\,|\,I(\omega-\omega')\,|\,I_{\gamma'}\mu\rangle\ , \tag{5.8}$$

where F is given by Eq. (5.7) with $d=0$ so that the λ summation is omitted. The Cooper pairs are formed from states in the immediate vicinity of the Fermi surface $\epsilon_F=\epsilon(\mathbf{k}_F)$, so that $F(\mathbf{k}_F)$ is of some interest. For a given representation i_γ, $F(\mathbf{k}_F)$ is determined by the contributions of the one-electron orbitals, $w_{i\mu_1}$ and $w_{j\mu_2}$, to the Cooper pairs at ϵ_F. When only one orbital symmetry, say $i=j=\Gamma_7$, determines the Bloch states at ϵ_F, then only the one-dimensional representations $\Gamma_1^\pm$ of D_{6h} occur as the symmetries of the cell-pair orbitals. Hence, no two-dimensional representations are met with, and no exotic superconducting phases occur. The negative parity representation Γ_1^- exists, however. The corresponding F is

$$\begin{aligned}F(\mathbf{k}_F,\rho\rho';\Gamma_1^\pm)=\tfrac{1}{2}\{&[a^*_{7+,-\tau/2}(\mathbf{k}_F\rho)a^*_{7-,-\tau/2}(-\mathbf{k}_F\rho')-a^*_{7-,-\tau/2}(\mathbf{k}_F\rho)a^*_{7+,-\tau/2}(-\mathbf{k}_F\rho')]\\&\pm[a^*_{7+,\tau/2}(\mathbf{k}_F\rho)a^*_{7-,\tau/2}(-\mathbf{k}_F\rho')-a^*_{7-,\tau/2}(\mathbf{k}_F\rho)a^*_{7+,\tau/2}(-\mathbf{k}_F\rho')]\}\ .\end{aligned} \tag{5.9}$$

From this equation it is clearly seen that the odd-parity state Γ_1^- owes its existence to the nonsymmorphic crystal structure of UPt$_3$. The Cooper pair consists of a linear combination of the two contact pairs centered at the two U sites in the unit cell. The sites are separated by a nonprimitive translation τ and have a center of inversion between them, Fig. 1. The above result arises as a consequence of the crystal symmetry; its form is anticipated in a paper by Anderson.[20] It is also clearly established here that—because of the $\mathbf{k}_F$ dependence of the function F given by Eq. (5.9)—it is unlikely that any simple model of the order parameter, $\Delta_{\rho\rho'}(\mathbf{k}_F)$, is at all relevant to the observations in heavy-fermion superconductors. The expli-

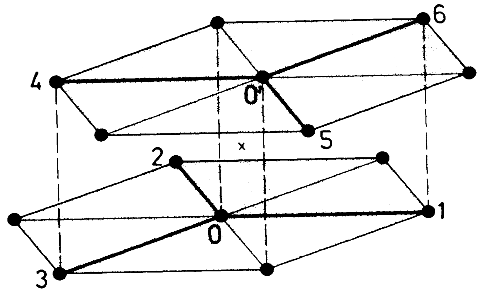

FIG. 7. The twelve next-nearest-neighbor sites participating in the formation of the cell orbital.

TABLE XIII. Symmetries of one-electron orbitals, contact pairs, nearest-neighbor, and next-nearest-neighbor pairs. The irreducible representations of D_{6h} in our notation and that of Ref. 4 are, respectively, Γ_1^+, A_{1g}; Γ_1^-, A_{1u}; Γ_2^+, A_{2g}; Γ_2^-, A_{2u}; Γ_3^+, B_{1g}; Γ_3^-, B_{1u}; Γ_4^+, B_{2g}; Γ_4^-, B_{2u}; Γ_5^+, E_{2g}; Γ_5^-, E_{2u}; Γ_6^+, E_{1g}; Γ_6^-, E_{1u}. We note that in the case $i=j$ the pair orbital Γ_2^+ for nearest-neighbor pairs does not occur [cf. the comments following Eq. (4.25)]. Similarly, for $i=j$ the pair orbital Γ_2 does not occur for next-nearest-neighbor pairs.

		Nearest-neighbor pairs		Next-nearest-Neighbor pairs	
One-electron orbitals point symmetry D_{3h}	Contact cell pairs Symmetry $D_{6h}=D_{3h}\cdot C_i$	Pair orbital at fixed pair of sites $\mathscr{S}=C_i\cdot C_s'$	Cell pairs symmetry $D_{6h}=\mathscr{S}\cdot C_{3h}$	Pair orbital at fixed pairs of sites $\mathscr{S}=C_{3v}$	Cell pairs symmetry $D_{6h}=\mathscr{S}\cdot C_i\cdot C_3$
Γ_7,Γ_7	$\Gamma_1^\pm$				
Γ_8,Γ_8	$\Gamma_1^\pm$	$\Gamma_1^\pm$	$\Gamma_1^\pm,\Gamma_3^\pm$ $\Gamma_5^\pm,\Gamma_6^\pm$	Γ_1	$\Gamma_1^\pm,\Gamma_5^\pm$
Γ_9,Γ_9	$\Gamma_1^\pm$			Γ_2	$\Gamma_3^\pm,\Gamma_6^\pm$
Γ_7,Γ_8	$\Gamma_3^\pm,\Gamma_4^\pm,\Gamma_5^\pm$			Γ_3	$\Gamma_2^\pm,\Gamma_5^\pm$
Γ_7,Γ_9	$\Gamma_5^\pm,\Gamma_6^\pm$	$\Gamma_2^\pm$	$\Gamma_2^\pm,\Gamma_4^\pm$ $\Gamma_5^\pm,\Gamma_6^\pm$	Γ_4	$\Gamma_4^\pm,\Gamma_6^\pm$
Γ_8,Γ_9	$\Gamma_5^\pm,\Gamma_6^\pm$				

cit **k** dependence of F is determined by the expansion coefficients $a_{i\mu,\tau/2}(\mathbf{k}_F,\rho)$ which can be found from band-structure calculations.

In the case where different orbital symmetries, say Γ_7 and Γ_8, admix into the Bloch waves at $\mathbf{k}_F$, then also the two-dimensional representations occur for the eigenfunctions, cf. Table III for the contact pairs. When we go beyond the contact model and take into account the nearest-neighbor and next-nearest-neighbor pairs, then all of the representations of D_{6h} occur for the eigenfunctions as is directly seen from Table XIII.

Equation (5.1) is the exact linearized gap equation; there is no restriction on the strength of the pairing interaction, Eq. (5.5). If the interaction is of electronic origin, as discussed in Ref. 21, the value of T_c/T_F may not be very small. When the frequency dependence of the order parameter becomes important, Eq. (5.1) can be generalized in the manner of the strong-coupling theory of superconductivity.[22]

VI. CONNECTION TO THE BLOCH-WAVE (k) REPRESENTATION

Let us assume that the solution of the T_c equation in the atomic representation Eq. (5.1) has provided us with the set of eigenfunctions $g(d,i_\gamma\mu)$ that yield the highest transition temperature. The corresponding Cooper pairs transform according to an irreducible representation i_G, i.e., $i_\gamma=\{i_G,\gamma\}$. We can readily transform this result into the **k** representation in order to obtain the Fermi-surface symmetry of the superconducting state at and just below T_c. For one-dimensional representations i_G, this transformation yields the desired **k**-space symmetry of the superconducting state. For multidimensional representations, we can make use of the results of other authors to determine the symmetry of the superconducting state near t_c.[4–6]

Assuming for simplicity that Cooper pairing occurs between mates in the same subband, we write the vertex eigenfunction in terms of Bloch waves as

$$\Gamma(\mathbf{r}s,\mathbf{r}'s')=\sum_{\mathbf{k},\rho,\rho'}\psi_{\mathbf{k}\rho}(\mathbf{r}s)\psi_{-\mathbf{k}\rho'}(\mathbf{r}'s')g_{\rho\rho'}(\mathbf{k})\ , \tag{6.1}$$

where $g_{\rho\rho'}(\mathbf{k})$ is the eigenfunction in **k** space. By comparing Eq. (6.1) with (2.8) we get the relation between the g's in the **k** and the **n** representations, in terms of the basic pairs, $g(\mathbf{n}+\tau_1-\tau_2;\ i_1\mu_1,i_2\mu_2)$. Substituting for the latter functions the symmetrized vertex functions of Eq. (3.17), we have

$$g_{\rho\rho'}(\mathbf{k})=\sum_{d}\sum_{i,\gamma,\mu}F(\mathbf{k},\rho\rho';d,i_\gamma\mu)g(d,i_\gamma\mu)\ , \tag{6.2}$$

where $i=i_G$ and F is defined by Eq. (5.7). There is a one-to-one correspondence between the eigenfunctions of the **k** representation transforming according to i_G,

$$g_{\rho\rho'}(\mathbf{k};i_G\mu) \tag{6.3}$$

and the functions,

$$\sum_{d}\sum_{\gamma}F(\mathbf{k},\rho\rho';d,i_\gamma\mu)g(d,i_\gamma\mu)\ , \tag{6.4}$$

determined by the eigenfunctions g.

The eigenfunctions of the **k** representation $g_{\rho\rho'}(\mathbf{k};i_G\mu)\equiv\Delta_{\rho\rho'}(\mathbf{k};i_G\mu)$ are discussed elsewhere.[2–6] At $T=0$, it is the order parametr in the **k** representation that corresponds in coordinate space to the usual wave function of a Cooper pair, the dimension of which is determined by the coherence length ξ. This wave function can be thought of as a coherent superposition of our cell pair orbitals, in analogy to a Bloch wave being a coherent superposition of the Wannier orbitals of each unit cell. Hence, within the length ξ there are many cell pairs, the dimension of which is governed by the short range of the e-e interaction and the Wannier orbitals.

VII. SUMMARY

Recently, the symmetry of heavy-fermion superconductors has been discussed in the Bloch (**k**) representation. This discussion leads to the classification of the possible superconducting singlet and triplet states into which the normal state transfers at and directly below T_c.[23] For each state, the particular **k**-space symmetry at ϵ_F determines the behavior of the equilibrium and transport phenomena in the superconducting phase.

Here, we take a different point of view and construct the Cooper-pair states in the atomic representation, that is, in terms of Wannier orbitals that take into account the periodic spin-orbit coupling effects. The motivation for this approach lies in the fact that the f electrons responsible for the heavy-fermion superconductivity are highly localized in space and spend most of their time at the f-atom sites. Besides, the pairing interaction is of short range in coordinate space whether phonons or spin fluctuations or both are responsible for the attractive interaction I between the electrons. As for ordinary phonons and their deformation-potential coupling to the electrons, I is governed by the short range of the phonon Green's function.[1] The local nature of I also holds for the breathing-mode coupling of the volume strain to the f electrons. This coupling is used in Ref. 7 to explain singlet superconductivity in the Ce compound; its importance for the elastic properties of U compounds is discussed by Yoshizawa *et al.*[24] As for ordinary paramagnons in homogenoeus systems, the range of I is determined by the spin-correlation length ρ that is rather short in Pd and in UAl_2.[25] A self-consistent paramagnon model is also applied to UPt_3 and accounts for the electronic specific heat.[21] For the Anderson lattice, the wave-vector dependence of the susceptibility, and hence ρ, is still unknown at low T.[26]

For the reasons given above, we develop the T_c eigenvalue equation for heavy fermions in the atomic representation. The goal is to determine, first of all, the parity and the symmetry of the superconducting state into which the normal metal transfers *and* to obtain the actual **k**-space symmetry of this state at ϵ_F by the transformation, Eq. (6.2). In contrast to ^{3}He, this symmetry is not merely a reflection of the physical nature of the pairing interaction. Instead, as we show in Secs. III and IV, the *crystal symmetry* plays an important role for the existence of even- and odd-parity states and their symmetry behavior. The reason is the presence of an inversion center between two U atoms in a *nonsymmorphic* lattice. Furthermore, the importance of *band-structure* effects for the existence of nontrivial superconducting states becomes evident in the *contact model,* cf. Table XIII. The possible existence of Γ_3 and Γ_4 as well as the two-dimensional representations depends on the admixture of different Wannier orbitals $w_{i\mu}(\mathbf{r},s)$ into the Bloch waves at ϵ_F. Because of these facts, the construction of the symmetrized pair orbitals or, equivalently, of the eigenfunctions in Secs. III and IV is straightforward, but complex. A reliable calculation of the highest T_c value is a difficult problem. However, based on a realistic pairing interaction I, the method developed in Sec. III can be applied to find the relative magnitudes of the T_c's for different symmetries.

This discussion presents a first step in this direction; we symmetirze the Cooper-pair orbitals and the corresponding vertex equations for T_c. The general procedure presented in Sec. III is applied to the $5f$ electrons of UPt_3 in Sec. IV. For the contact model where the two mates reside at one and the same site, the odd-parity state Γ_1^- always occurs, by virtue of the inversion center between the two U atoms. The **k** dependence for the eigenfunction of the Γ_1^- contact state is given by Eq. (5.9). It is unlikely that this dependence resembles one of the four simple solutions to the triplet gap functions of ^{3}He. In the case of nearest-neighbor pairs, the two mates of a cell (symmetrized) pair orbital reside at one of the U-atom pairs shown in Fig. 5. Although there is no direct overlap between two neighbor U atoms (4.15 Å apart), the orthogonalization of the $5f$ orbital at site 1 to the $6d$ orbital at site 2, and vice versa, leads to some indirect overlap between the $5f$ states. Perhaps more important, there is significant hybridization between the $5f$ orbitals and the $5d$ orbitals of the Pt atoms. All of the representations of the group D_{6h} occur as the possible symmetries of the nearest-neighbor pairs, cf. Table VIII. Each U atom has six next-nearest neighbors, each at a distance of 5.8 Å. The cell orbital consists of a linear superposition of twelve electron pairs, Eq. (4.32), each of which occupies one of the equivalent atom pairs shown in Fig. 7. These NNN pair orbitals can become involved in superconductivity if there is a sufficiently strong hybridization between the U $5f$ and the Pt $6d$ electrons at ϵ_F. The Pt atoms lie between the U atoms as seen in Fig. 1. All of the symmetries of contact, nearest-neighbor, and next-nearest-neighbor pairs are found in Table XIII.

The second step, namely the actual solution of the T_c eigenvalue equation requires the input of some realistic model for the quasiparticle band structure and for the pairing interaction I. Then, using the symmetrization procedure developed here for Cooper pairs consisting of tightly bound spin-orbit electrons, one can attempt to find the actual parity and symmetry of the heavy fermions in a metallic superconductor.

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APPENDIX A: NEAREST-NEIGHBOR PAIR ORBITALS $\mathscr{f}(i_S)$

To find $\mathscr{f}(i_S)$, Eq. (4.23), let us consider the projection of this product set $w_{7\mu}(\mathbf{r}+\tau/2,s)w_{7\nu}(\mathbf{r}'-\tau/2,s')$ into the representations Γ_1 and Γ_2 of $C_s'=S$. We have

$$\begin{aligned} P^{(\Gamma_1)}w_{7+}w_{7+} &= \tfrac{1}{4}(E+\bar{E}+\sigma_{v_2}+\bar{\sigma}_{v_2})w_{7+}w_{7+} \\ &= \tfrac{1}{2}(w_{7+}w_{7+}-\epsilon^* w_{7-}w_{7-}) \\ &= \frac{\epsilon}{2}(\epsilon^* w_{7+}w_{7+}-\epsilon w_{7-}w_{7-}), \quad \epsilon \equiv e^{2\pi i/3} . \end{aligned} \tag{A1}$$

This linear combination is clearly invariant under the symmetry operations of C_s'. We are free to choose a phase factor so that the above orbital does not change its sign under K, cf. Eq. (4.20). Hence

$$\mathscr{f}\left(\mathbf{r}+\frac{\tau}{2},s;\mathbf{r}'-\frac{\tau}{s},s';\Gamma_1^b\right)=\frac{i}{\sqrt{2}}\left[\epsilon^* w_{7+}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{7+}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]-\epsilon w_{7-}\left[\mathbf{r}+\frac{\tau}{2},s\right]w_{7-}\left[\mathbf{r}'-\frac{\tau}{2},s'\right]\right] \tag{A2}$$

and

$$K\mathscr{f}(\Gamma_1^b)=\mathscr{f}(\Gamma_1^b)\ . \tag{A3}$$

The second pair orbital transforming according to Γ_1 of C_s' is obtained by applying $P^{(\Gamma_1)}$ to $w_{7+}w_{7-}$,

$$\begin{aligned}P^{(\Gamma_1)}w_{7+}w_{7-}&=\tfrac{1}{4}(E+\bar{E}+\sigma_{v_2}+\bar{\sigma}_{v_2})w_{7+}w_{7-}\\&=\tfrac{1}{2}(w_{7+}w_{7-}-w_{7-}w_{7+})\\&=\sqrt{2}\mathscr{f}(\Gamma_1^a)\ .\end{aligned} \tag{A4}$$

For the two Γ_2 representations we get

$$\begin{aligned}P^{(\Gamma_2)}w_{7+}w_{7+}&=\frac{i\epsilon}{2}(\epsilon^* w_{7+}w_{7+}+\epsilon w_{7-}w_{7-})\\&=\sqrt{2}\mathscr{f}(\Gamma_2^b)\end{aligned} \tag{A5}$$

and

$$\begin{aligned}P^{(\Gamma_2)}w_{7+}w_{7-}&=\tfrac{1}{2}(w_{7+}w_{7-}+w_{7-}w_{7+})\\&=\sqrt{2}\mathscr{f}(\Gamma_2^a)\ .\end{aligned} \tag{A6}$$

APPENDIX B: NEAREST-NEIGHBOR CELL ORBITALS

The six pair orbitals given by Eq. (4.26) form the basis set of a six-dimensional vector space. By applying the projection operator,

$$P_{\mu\rho}^{(i_{3h})}=\frac{d}{n}\sum_R D_{\mu\rho}^{(i_{3h})^*}(R)R\ , \tag{B1}$$

to the orbital $\mathscr{f}(i_{\mathscr{S}})$, Eq. (4.25), we generate six orthogonal vectors, the cell orbitals. The matrices $D_{\mu\rho}^{(i_{3h})}$ are given by Table I. To find the projection of $P^{(i_{3h})}$ on $\mathscr{f}(i_{\mathscr{S}})$, we use the group properties of D_{6h}; for example, $\sigma_{v_1}=C_3^+\sigma_{v_2}$. For $\mathscr{f}(i_{\mathscr{S}}=\Gamma_1)$ we get

$$\begin{aligned}P^{(\Gamma_1)}\mathscr{f}&=\tfrac{1}{12}(E+C_3^+ +C_3^- +\sigma_h+S_3^+ +S_3^-)(1+\sigma_{v_2})\mathscr{f}\\&=\tfrac{1}{6}(\mathscr{f}_1+\mathscr{f}_2+\mathscr{f}_3+\mathscr{f}_4+\mathscr{f}_5+\mathscr{f}_6)\ ,\end{aligned} \tag{B2}$$

where it is taken into account that $\sigma_{v_2}\mathscr{f}(\Gamma_1)=\mathscr{f}(\Gamma_1)$. Furthermore,

$$P^{(\Gamma_2)}\mathscr{f}=0\ , \tag{B3}$$

$$\begin{aligned}P^{(\Gamma_3)}\mathscr{f}&=\tfrac{1}{12}(E+C_3^+ +C_3^- -\sigma_h-S_3^+ -S_3^-)(1+\sigma_{v_2})\mathscr{f}\\&=\tfrac{1}{6}(\mathscr{f}_1+\mathscr{f}_2+\mathscr{f}_3-\mathscr{f}_4-\mathscr{f}_5-\mathscr{f}_6)\ ,\end{aligned} \tag{B4}$$

$$P^{(\Gamma_4)}\mathscr{f}=0\ , \tag{B5}$$

$$\begin{aligned}P_{11}^{(\Gamma_5)}\mathscr{f}&=\tfrac{1}{6}(E+\epsilon C_3^+ +\epsilon^* C_3^- +\sigma_h+\epsilon S_3^+ +\epsilon^* S_3^-)\mathscr{f}\\&=\tfrac{1}{6}(\mathscr{f}_1+\epsilon\mathscr{f}_2+\epsilon^*\mathscr{f}_3+\mathscr{f}_4+\epsilon\mathscr{f}_5+\epsilon^*\mathscr{f}_6)\ ,\end{aligned} \tag{B6}$$

$$\begin{aligned}P_{21}^{(\Gamma_5)}\mathscr{f}&=\tfrac{1}{6}(E+\epsilon^* C_3^+ +\epsilon C_3^- +\sigma_h+\epsilon^* S_3^+ +\epsilon S_3^-)\epsilon\sigma_{v_2}\mathscr{f}\\&=\frac{\epsilon}{6}(\mathscr{f}_1+\epsilon^*\mathscr{f}_2+\epsilon\mathscr{f}_3+\mathscr{f}_4+\epsilon^*\mathscr{f}_5+\epsilon\mathscr{f}_6)\ ,\end{aligned} \tag{B7}$$

$$\begin{aligned}P_{11}^{(\Gamma_6)}\mathscr{f}&=\tfrac{1}{6}(E+\epsilon C_3^+ +\epsilon^* C_3^- -\sigma_h-\epsilon S_3^+ -\epsilon^* S_3^-)\mathscr{f}\\&=\tfrac{1}{6}(\mathscr{f}_1+\epsilon\mathscr{f}_2+\epsilon^*\mathscr{f}_3-\mathscr{f}_4-\epsilon\mathscr{f}_5-\epsilon^*\mathscr{f}_6)\ ,\end{aligned} \tag{B8}$$

$$\begin{aligned}P_{21}^{(\Gamma_6)}\mathscr{f}&=\frac{\epsilon}{6}(-E-\epsilon^* C_3^+ -\epsilon C_3^- +\sigma_h+\epsilon^* S_3^+ +\epsilon S_3^-)\sigma_{v_2}\mathscr{f}\\&=\tfrac{1}{6}(-\mathscr{f}_1-\epsilon^*\mathscr{f}_2-\epsilon\mathscr{f}_3+\mathscr{f}_4+\epsilon^*\mathscr{f}_5+\epsilon\mathscr{f}_6)\ .\end{aligned} \tag{B9}$$

These orbitals present the correct linear combinations of the functions $\mathscr{f}_\lambda(i_{\mathscr{S}}=\Gamma_1)$ which transform according to the irreducible representations of D_{6h}. Since D_{6h} is the set product—and not the direct product—of C_{3h} and $\mathscr{S}$ the group elements of C_{3h} and $\mathscr{S}$ do not commute with each other. We can use, however, the multiplication properties in order to commute the elements of C_{3h} with σ_{v_2} of $\mathscr{S}$, for example, $\sigma_{v_2}C_3^+=C_3^-\sigma_{v_2}$. For $i_{\mathscr{S}}=\Gamma_2$, we get the cell orbitals in the same manner as for $i_{\mathscr{S}}=\Gamma_1$, taking into account that $\sigma_{v_2}\mathscr{f}(\Gamma_2)=-\mathscr{f}(\Gamma_2)$.

APPENDIX C: THE KERNEL $\mathscr{K}$

The right-hand side of Eq. (5.8) for the kernel $\mathscr{K}$ contains the anomalous Green's function GG and the pairing interactions I in terms of the cell orbitals for the Cooper pairs. We now proceed to express GG and I in terms of the basic pairs, Eq. (3.2).

The Green's function is given by

$$\begin{aligned}\langle d,i_\gamma\mu\,|\,G(\omega)G(-\omega)\,|\,d',i_{\gamma'}\mu\rangle&=\int d\tau_1\cdots\int d\tau_4\mathscr{f}^*(\mathbf{r}_1,\mathbf{r}_2;d,i_\gamma\mu)G(\mathbf{r}_1,\mathbf{r}_3;\omega)\\&\quad\times G(\mathbf{r}_2,\mathbf{r}_4;-\omega)\mathscr{f}(\mathbf{r}_3,\mathbf{r}_4;d'i_{\gamma'}\mu)\ ,\end{aligned} \tag{C1}$$

where $\mathbf{r}=\{x,y,z;s\}$ and $d\tau=d\tau(x,y,z;s)$; the degeneracy index depends on the symmetries i and j of the basic pair, $\gamma=\{\gamma;i,j\}$. In the atomic representation, Eq. (C1) becomes

$$\langle\,|\,GG\,|\,\rangle=\sum_{1,2,3,4}F^*(1,2\,|\,d,i_\gamma\mu)G(1,3;\omega)\times G(2,4;-\omega)F(3,4;d',i_{\gamma'}\mu)\ , \tag{C2}$$

where, e.g., $1=\{\mathbf{n}_1,\tau_1,i_1\mu_1\}$ and F denotes the inner product,

$$\begin{aligned}F(1,2;d,i_\gamma\mu)&=\int d\tau\int d\tau' w_{i\mu_1}^*(\mathbf{r}-\mathbf{n}_1-\tau_1)\\&\quad\times w_{j\mu_2}(\mathbf{r}'-\mathbf{n}_2-\tau_2)\mathscr{f}(\mathbf{r},\mathbf{r}';d,i_\gamma\mu)\\&=C_{\mu_1\mu_2\mu}^{iji_\gamma}\delta_{\mathrm{d},\mathbf{n}_1+\tau_1-\mathbf{n}_2-\tau_2}\delta_{i_1 i}\delta_{i_2 j}\ .\end{aligned} \tag{C3}$$

We use this equation and the translational invariance of G to write Eq. (C2) as

$$\langle \,|\, GG \,|\, \rangle = \sum_{\mu_1 \cdots \mu_4} \sum_{\kappa\lambda,\kappa'\lambda'} C^{i_1 i_2 i_\gamma^*}_{\mu_1\mu_2\mu} C^{i_3 i_4 i_{\gamma'}}_{\mu_3\mu_4\mu} \times N_0 \sum_{\mathbf{d}_{23}} G(\mathbf{d}'+\mathbf{d}_{23},\omega) \times G(\mathbf{d}+\mathbf{d}_{23},-\omega) \,, \tag{C4}$$

where $\mathbf{d}_{23}=\mathbf{n}_2+\tau_2-\mathbf{n}_3-\tau_3$ and the orbital indices of the G's correspond to those of Eq. (C2). The one-electron Green's function is

$$G(\mathbf{d}_{12};i_1\mu_1,i_2\mu_2)=\frac{1}{N_0}\sum_{\mathbf{k},\rho} e^{i\mathbf{k}\cdot\mathbf{d}_{12}} \frac{a_{i_1\mu_1,\tau_1}(\mathbf{k}\rho)a^*_{i_2\mu_2,\tau_2}(\mathbf{k}\rho)}{\epsilon-\epsilon_\rho(\mathbf{k})} \,. \tag{C5}$$

When the Green's function, Eq. (C5), is substituted for G in (C4) we arrive at Eq. (5.6).

In an analogous manner, the pairing interaction I of Eq. (5.5) can be found in terms of the interaction between basic pairs; the result is

$$\langle d,i_\gamma\mu \,|\, I(\omega-\omega') \,|\, d',i\gamma'\mu \rangle = N_0 \sum_{\mu_1 \cdots \mu_4} \sum_{\lambda\kappa,\lambda'\kappa'} C^{i_1 i_2 i_\gamma^*}_{\mu_1\mu_2\mu} C^{i_3 i_4 i_\gamma}_{\mu_3\mu_4\mu} \times \sum_{\mathbf{d}_{32}} \langle 0,i_1\mu_1;\mathbf{d}',i_2\mu_2 \,|\, I \,|\, \mathbf{d}_{32}+\mathbf{d}',i_3\mu_3;\mathbf{d}+\mathbf{d}'+\mathbf{d}_{32},i_4\mu_4 \rangle \,. \tag{C6}$$

Note that, for example, $\mathbf{d}=\{d,\lambda,\kappa\}$.

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