# What do we know for sure about the cuprate superconductors? II. Symmetry of the order parameter.*

If we consider a gas of weakly interacting fermions in free space, with a BCS-type pairing interaction $V_{\mathbf{k}\mathbf{k}'}$ for states close to the Fermi surface such that $V_{\mathbf{k}\mathbf{k}'}$ is not a strong function of $|\mathbf{k}|$ and $|\mathbf{k}'|$ but may be a strong function of the angle $\mathbf{k}\cdot\mathbf{k}'$ between them, then the resulting BCS gap equation takes the form†

$$\Delta_{\mathbf{k}} = -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} \tanh \frac{E_{\mathbf{k}'}}{2T} \tag{1}$$

and it is known that as well as (possibly) the familiar original BCS solution, namely $\Delta_{\mathbf{k}}$=const, there may, depending on the form of $V_{\mathbf{k}\mathbf{k}'}$ also solutions in which $\Delta$ is a function of direction on the Fermi surface: $\Delta = \Delta(\mathbf{k})$. (Solutions even in $\mathbf{k}$ correspond to a spin singlet pairing, while these corresponding to $\Delta$ odd in $\mathbf{k}$ correspond to spin triplet state). Such solutions are not generally believed to be realized in the classic superconductors, but it is almost universally believed that the pairing scheme corresponding to each of the three superfluid phases of $^3$He is of this type, and strongly suspected that a similar situation occurs also in some heavy-fermion systems and in $SrRu_2O_4$. Formally, these situations, which I shall call 'exotic', differ from the ('conventional') BCS pairing scheme in that order parameter $\langle a^\dagger_{\mathbf{k}\alpha} a^\dagger_{-\mathbf{k}\beta}\rangle$ transforms according to a nontrivial representation (or a combination of such) of the symmetry group of the Hamiltonian (in the case of free space, $SO(3)_{\rm orb} \otimes SU(2)_{\rm spin}$). From the very earliest days of work on the cuprates, it has been an important question whether the pairing state realized there is 'conventional' or 'exotic' (and if the latter, of what type), and although a strong consensus has been reached in recent years, the battle is still not quite over.

It is important to realize that the question of the symmetry of the order parameter can be discussed quite independently of the validity or not of the BCS (weak-coupling) approach: the only assumption we need is the existence of ODLRO, on which see lecture 9. Formally, we assume that for some values of $t_1, \ldots, t_4$ we have

$$\langle \psi^\dagger_\alpha(\mathbf{r}_1 t_1)\psi^\dagger_\beta(\mathbf{r}_2 t_2)\psi_\gamma(\mathbf{r}_3 t_3)\psi_\delta(\mathbf{r}_4 t_4)\rangle = \begin{cases} = 0, & T > T_c \\ = \text{const}, & T < T_c \end{cases} \tag{2}$$

in the limit‡ $|\mathbf{r}_1 + \mathbf{r}_2 - \mathbf{r}_3 - \mathbf{r}_4| \to \infty$, $|\mathbf{r}_1 - \mathbf{r}_2|$ and $|\mathbf{r}_3 - \mathbf{r}_4|$ finite and fixed. This then allows us to define an 'anomalous average' of the standard form

$$F_{\alpha\beta}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \equiv \langle \psi_\alpha(\mathbf{r}_1 t_1)\psi_\beta(\mathbf{r}_2 t_2)\rangle \tag{3}$$

with the usual assumption of relaxation of particle number conservation. Except for one very special possibility (namely that $F$ is odd in the interchange of $t_1$ and $t_2$) which

*Ref: Annett et al., in G V.

†Since this discussion is only motivational, I ignored some of the complications associated with spin triplet pairing (see lecture 1)

‡The definition strictly needs to be tightened up a little to allow for the possibility that $F$ depends nontrivially on the COM coordinate $(\mathbf{r}_1 + \mathbf{r}_2)/2$.

seems very unlikely to be relevant to the cuprates,[§] $F$ will, barring pathology, have a finite value at $t_1 = t_2$, and we use this to define a generalized Ginzburg-Landau type order parameter by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha, \beta) \equiv \langle \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2)\rangle = -\Psi(\mathbf{r}_2, \mathbf{r}_1; \beta, \alpha) \ \left[ \equiv F_{\alpha\beta}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)_{t_1=t_2}\right] \quad (4)$$

It is the symmetry of the order parameter $\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha, \beta)$ which is the subject of the ensuing discussion; it should be carefully noted that in any theory more general than a simple BCS-type weak coupling theory there need not be any simple relationship between $\Psi$ and the single-particle energy gap (even if the latter concept is unambiguously defined, which it may not be). In particular, the fact that $\Psi$ vanishes for certain direction on the Fermi surface (if this concept is applicable, see below) need not imply that $|\Delta|$ also vanishes there.

In general, the group $G$ of exact symmetry of the Hamiltonian of a cuprate superconductor is of the form

$$G = U(1) \otimes T_l \otimes H \quad (5)$$

where $U(1)$ is the usual gauge group. $T_l$ is the (abelian) group of lattice translations and $H$ is the point group of the crystal in question. Although it is possible to give a general analysis, life simplifies enormously if we make the 'default' assumption that the symmetry with respect to $T_l$ is not broken in the superconducting state, i.e., that the order parameter transforms according to the trivial (identity) representation of $T_l$. At present there seems no convincing evidence against this 'default' hypothesis[¶] Thus, we can in effect take $G$ to be given by $U(1) \otimes H$. We know that the symmetry with respect to $U(1)$ is spontaneously broken (in the usual sense of the BCS 'particle-nonconserving' trick): is that with respect to $H$ also broken?

If we could neglect spin-orbit coupling, $H$ could be written as a product $SU(2)_{\rm spin} \otimes H^*_{\rm orb}$ where $H^*_{\rm orb}$ is a group containing reflections, rotations etc. of the orbital coordinates only. Since spin-orbit coupling is not totally negligible for the cuprates, we must rather take the group as consisting of such orbital operations coupled with similar operations on the spin space. However, at this point life again simplifies enormously if we make the assumption of spin singlet pairing, namely

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha, \beta) = (i\sigma_y)_{\alpha\beta}\Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (6)$$

If this is right, then the symmetry group is reduced effectively to $U(1) \otimes H_{\rm orb}$.

Equation (6), while extremely plausible, is perhaps not 100% foolproof. The principal justification for it is the experimental observation, by now made in many different cuprate superconductors, that the Knight shift (or more accurately its 'Pauli' part) tends to zero in the superconducting state in the limit $T \to 0$, independently of the field direction. In any simple weak-coupling theory of the BCS type, this behavior would be unambiguous

[§] See Annett et al., ref. cit., p. 387.

[¶] Despite the currently fashionable emphasis on the 'stripes' which have been verified to exist in particular regimes of the phase diagram for one or two super conducting cuprates, there is to my mind no evidence that they are a generic feature, let alone that they have anything to do with superconductivity.

evidence of spin singlet pairing. It may perhaps be argued that in a more general theory we cannot be absolutely sure that a triplet-paired (or perhaps mixed singlet-triplet) state would not behave in the same way, but to the best of any knowledge no concrete theory having this property has been proposed, and while effects beyond BCS might lead to some reduction in $K_s$ (cf. also the behavior of $^3$He-B) it seems a priori very implausible that they would lead to its complete vanishing. Thus from now on, I will assume that equation (6) is correct for the cuprates, whereupon it follows from the Pauli principle that $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ has even parity, i.e., is symmetric in $\mathbf{r}_1$ and $\mathbf{r}_2$. The question at issue therefore reduces to the symmetry of $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ under the operations of the 'orbital' point group $H_{\rm orb}$ of the relevant crystal.

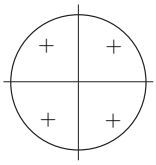
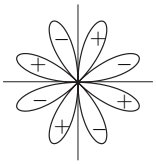
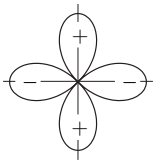
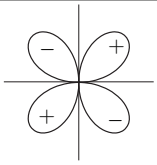
Let us for the moment neglect the complications associated with the c-axis layering structure and thus restrict $\mathbf{r}_1$ and $\mathbf{r}_2$ to lie within a single $CuO_2$ plane. Although the ensuing argument is quite general, it helps one's intuition if one also fixes the center-of-mass coordinate $(\mathbf{r}_1 + \mathbf{r}_2)/2$ to lie at a point of high symmetry in the lattice, let us say the position of a Cu atom. (A similar simplification is obtained if one assumes that relevant electron states come from a single band, so that the quantity $F_{\mathbf{k}} \equiv \langle a^\dagger_{\mathbf{k}\uparrow} a^\dagger_{-\mathbf{k}\downarrow} \rangle$ is unambiguous defined (with $\mathbf{k}$ the appropriate Bloch quasimomentum; then the relevant question is the symmetry of $F_{\mathbf{k}}$ under operations of $H_{\rm orb}$ on $\mathbf{k}$. I shall generally not distinguish explicitly between the $\mathbf{r}$-space and $\mathbf{k}$-space representations of the order parameter, since from the point of view of symmetry classification (only!) they are essentially identical). If we neglect for the moment yet another complication, namely that of orthorhombic anisotropy (which is small or zero in most materials other than YBCO), then the symmetry group of the $CuO_2$ planes is that of the square, namely $C_{4v}$ in the standard group-theoretical terminology. This is a rather simple group: the primitive operations are

(a) rotation through $\pi/2$ about the (001)($z$-) axis ($\hat{R}_{\pi/2}$)

(b) reflection in a crystal axis, e.g. (100) ($\hat{I}_{\rm axis}$)

(c) and reflection in a 45° (110) axis ($\hat{I}_{\pi/4}$);

any one of these three can be represented as a product of the other two, i.e. $\hat{I}_{\rm axis}\hat{I}_{\pi/4}\hat{R}_{\pi/2} = 1$. In view of the above conclusion about the spin singlet nature of the pairing and the consequent even parity of the state, all states we are interested in here $\hat{R}^2_{\pi/2} = +1$, and moreover of course $\hat{I}^2_{\rm axis} \equiv \hat{I}^2_{\pi/4} \equiv +1$. Thus, all the even-parity irreducible representations can be labeled by the possible eigenvalues, $\pm 1$, of (e.g.) the operators $\hat{R}_{\pi/2}$ and $\hat{I}_{\rm axis}$. These four possible representations, which are all one-dimensional, are denoted $A_{1g}$ , $A_{2g}$ , $B_{1g}$ and $B_{2g}$ in the standard group-theoretic notation, or informally respectively as $s^+$, $s^-$ (or $g$), $d_{x^2-y^2}$ and $d_{xy}$; their symmetry properties are shown in the Table and correspond to the 'representative' functions shown; $A_{1g}$ is the 'identity' (or 'trivial' representation). Representative forms of the corresponding functions are also shown in the Table; however, it should be emphasized that the actual form may look quite different, provided only that it transforms in the correct way. For example, a possible form

| | Informal name | Group-theoretic notation | $\hat{R}_{\pi/2}$ | $\hat{I}_{\text{axis}}$ | Representative state |
|---|---|---|---|---|---|
|  | $s^+$ | $A_{1g}$ | $+1$ | $+1$ | const |
|  | $s^-$ ('$g$') | $A_{2g}$ | $+1$ | $-1$ | $xy(x^2-y^2)$ |
|  | $d_{x^2-y^2}$ | $B_{1g}$ | $-1$ | $+1$ | $x^2-y^2$ |
|  | $d_{xy}$ | $B_{2g}$ | $-1$ | $-1$ | $xy$ |

of $s$-wave OP as a function of the angle $\theta$ in the $CuO_2$ plane is $A + B\cos 4\theta$, which for $|B| > |A|$ has 8 nodes (such a form of OP is sometimes called on 'extended $s$-wave' state).

In general, the OP of a superconducting cuprate may correspond to a single irreducible representation ('irrep') of the group $C_{4v}$, or to a superposition of irreducible representations (the latter possibility is often labeled in shorthand (e.g.) '$s + id_{x^2-y^2}$' to indicate the representations involved). However, it is very important to appreciate that a very severe constraint on the latter possibility is placed by the experimentally observed thermodynamic behavior of the cuprates. To see this, we write down an expression for the Ginzburg-Landau free energy in terms of the amplitudes $\psi_i$ of the various irreducible representations: bearing in mind that the requirement of gauge invariance allows only equal number of $\psi$'s and $\psi^*$'s, we see that the most general expression up to terms of fourth order is:

$$F(T) = \sum_{ij} \alpha_{ij}(T)\psi_i^*\psi_j + \frac{1}{2}\sum_{ijkl}\beta_{ijkl}(T)\psi_i^*\psi_j^*\psi_k\psi_l \tag{7}$$

However, $F$ is required to be invariant under the operations not only of the gauge group $U(1)$ but also of the crystal point group, $H_{\rm orb}$ $(= C_{4v})$. Since any two different irreps differ in their eigenvalue under at least one operator of $C_{4v}$, it immediately follows that $\alpha_{ij}(T) \sim \delta_{ij}$ (this result is independent of the particular group). Furthermore, because of the particularly simple structure of the group $C_{4v}$, it follows that in the fourth-order term two different irreps can mix only 'two by two': in particular, terms of the form (e.g.) $|\psi_i|^2\psi_i^*\psi_j$ are forbidden,* as is any combination of three different $\psi_i$: only terms of the form $|\psi_i|^2|\psi_j|^2$ $(\sim A_1)$, and $\psi_i^*\psi_i^*\psi_j\psi_j$ $(\sim A_2)$ are allowed. Thus, if $\phi_{ij}$ denotes the relative phase of $\psi_i$ and $\psi_j$, the most general form of free energy for a system with the $C_{4v}$ symmetry is

$$F(T) = \sum_{i=1}^{4} \alpha_i(T)|\psi_i|^2 + \frac{1}{2}\sum_{ij=1}^{4} \beta_{ij}(T)|\psi_i|^2|\psi_j|^2 f(\phi_{ij}) \tag{8}$$

(where $f$ depends on the relative magnitude of the $A_1$ and $A_2$ terms, above). Now it is straightforward to show, within the standard mean-field treatment of the thermodynamics, that the transition to the superconducting phase occurs at the point where a particular one of the functions $\alpha_i(T)$ first becomes negative, and that immediately below this transition the only component represented is the corresponding $\psi_i$. Moreover, appearance of a second component at lower temperature requires a second phase transition, which depending on the relative magnitudes of the $\alpha$'s and $\beta$'s involved may be either second or first order,† and which, barring pathologies would be expected to give at least derivative discontinuities in just about all physical quantities. Now, with the possible but very dubious exception of a single fairly recent experiment on YBCO, there seems absolutely no evidence for such a second phase transition in any cuprate examined to date, and indeed plenty of evidence against it (in the sense that in many experiments quantities such as the penetration depth $\lambda(T)$ have been plotted carefully as a function of temperature from very low $T$ to $T_c$, and no anomalies found). Thus, the thermodynamic behavior of the cuprates provides very strong evidence that the OP of the bulk system belongs to a single irreducible representation of $C_{4v}$. (One cannot necessarily draw an equivalent conclusion concerning the OP near a surface (or perhaps in the vicinity of certain types of impurity), since the corresponding contribution to the thermodynamic quantities is likely to be so small relative to the bulk contribution as to be invisible in practice). Given this, the leading contenders for the bulk OP are a simple $s$-wave $(A_{1g})$ state, possibly of the 'extended' type, and the $d_{x^2-y^2}$ $(B_{1g})$ state.

Before embarking on a discussion of experimental tests, we should say a word about the complications due to orthorhombicity and c-axis structure. While the members of the Hg series are strictly tetragonal and those of the two Tl series very nearly so, most other cuprates have some orthorhombic asymmetry. In particular, in YBCO (both 1237 and 1248) the chains break the tetragonal symmetry, so that while $\hat{I}_{\rm axis}$ remains a good

*A term of the form $\psi_i^*\psi_j^*\psi_k\psi_l$ where $i, j, k, l$ are all different is allowed, but does not affect the subsequent argument. Note that these conditions do not hold for an arbitrary symmetry group (e.g. for $SO(3)$).

†For a detailed analysis see Y. Imry, J. Phys. C **8**, 567 (1975).

symmetry $\hat{R}_{\pi/2}$ and $\hat{I}_{\pi/4}$ are no longer so. In LSCO and the Bi series, on the other hand, it is the two orthogonal 45° axes which are inequivalent, while remaining mirror planes; thus in this case $\hat{I}_{\pi/4}$, but not $\hat{R}_{\pi/2}$ or $\hat{I}_{\rm axis}$, remains a good symmetry. As a result of the orthorhombicity, the states cannot be classified rigorously as (e.g.) $s$ or $d_{x^2-y^2}$; however, we can still classify them as '$s$-like' or '$d$-like' according as the OP preserves or changes its sign under a $\pi/2$ rotation (the magnitude will in general change, e.g., in YBCO it seems plausible that the OP along the b-axis will be greater in magnitude than that along the a-axis).

Most experiments on YBCO have been done on twinned crystals, and in interpreting these it is important to know how the OP, should it be $d_{x^2-y^2}$-like, behaves as we cross a twin boundary: does it preserve its sign with respect to the 'absolute' (NSEW) axes, or to the crystal a-and b-axes? For reasons given in Annett et al. (ref. cit., p. 391) I believe it is overwhelmingly plausible that the first ('gyroscopic') alternative is correct, i.e. that (e.g.) the + sign is everywhere associated with a N-S axis, irrespective of whether the crystal is oriented so that it is the a-axis or b-axis. (The magnitude of the corresponding component may of course depend on the latter).

Finally, what about the possible complications associated with the c-axis layering structure? In principle this gives rise to a large number of new possibilities, but all of them would require either that the pairing is exclusively inter-plane (i.e. that $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ vanishes when $\mathbf{r}_1$ and $\mathbf{r}_2$ lie in the same $CuO_2$ plane) or that reflection symmetry (in bilayer materials) and/or the translational symmetry under a c-axis lattice translation is broken. It seems difficult to reconcile either of these hypotheses either with the existence of an (ab-plane) Josephson effect between cuprates and classic superconductors, or with the apparent qualitative independence of the superconducting behavior from the c-axis structure. Nevertheless, since the most worrying objections to the 'established' symmetry assignment come from experiments sensitive to the c-axis behavior, we should at least bear these complications at the back of our minds.

I now turn to the question of experimental discrimination between the '$s$' and '$d$' (i.e. $d_{x^2-y^2}$) hypotheses. There exists by now a vast body of experiments, both spectroscopic and on the asymptotic temperature-dependence of quantities such as the penetration depth as $T \to 0$, which give apparently incontrovertible evidence that the single-particle density of states in a typical cuprate superconductor is nonzero down to an energy of at most of the order of $0.01T_c$. Unfortunately, this does not by itself rule out the $s$-wave scenario: all it tends to show is that the single-particle energy gap has nodes (or a least very low minima), and this is entirely consistent with an 'extended $s$-wave scenario'. A further difficulty in interpreting such experiments as giving information on the order parameter is that the very existence of the pseudogap phenomenon shows that we can get a thinning-out of the low-energy DOS even when the superconducting OP is zero, so that there is no one-one correspondence between the two quantities (although it is admittedly difficult to envisage a scenario where the OP is finite in all directions but the DOS at low or zero energy is nevertheless finite). A somewhat more promising class of evidence comes from the angular dependence of the 'gap' seen in the ARPES, which by now is universally agreed to be a maximum in the $(\pi, 0)$ direction (along the crystal

axes) and either zero of at least very small along the $(\pi, \pi)$ (45° diagonal) direction – exactly the behavior and would expect for a $d_{x^2-y^2}$ state if the amplitude of the gap as a function of angle reflects that of the OP. Again, the interpretation is complicated by the fact that

(a) the gap seen in ARPES may not be simply the 'superconducting' gap, and

(b) an extended $s$-wave state of the form (e.g.) $A + B\cos 4\theta$ with $B$ slightly greater than $A$, would give an angular dependence of $|\Delta|$ which might in practice be very difficult to distinguish from a $d_{x^2-y^2}$ state.

Clearly, the optimum way of distinguishing a $d$-state from an $s$-state would be by looking directly at its defining characteristic, namely the presence or absence of a sign change in the order parameter under a $\pi/2$ rotation. In principle, some spectroscopic experiments, e.g. Raman and neutron scattering, can give information on this point, because while the energies of the 'particle-hole' states excited are of course not directly sensitive to the presence or absence of the sign change the relevant coherence factors depend on it; see Annett et al., sections 5.3-4. However, the interpretation of such experiments requires a number of nontrivial further assumptions (typically, that the microscopic state of the pairs is reasonably 'BCS-like'), so I omit discussion of them and go on now to the one class of experiments which appears to be capable of determining the symmetry of the OP independently of microscopic assumptions, that is the Josephson (quantum phase interference) experiments. Such experiments were originally proposed in the context of the heavy-fermion superconductors, some of which are thought to be paired in a $p$-wave state (cf. lecture 1); however, for good practical reasons (cf. below) they were not attempted in this context until very recently. By contrast, in the case of the cuprates this kind of experiment has been spectacularly successful [1998 Buckley Prize].

In reading the (now extensive) literature on the Josephson experiments, it is important to distinguish between arguments which rely on certain implicit assumptions about tunneling matrix elements, etc., (e.g. the 'Sigrist-Rice' formula, see below) and those which are independent of such considerations and rely only on basic symmetry principles; I will concentrate on the latter, since I believe that it is only when this is done that the Josephson experiments have a unique status.

As we saw in part I, lecture 13, when two classic ($s$-wave) superconductors are coupled by a Josephson junction, this induces a (lowest-order) Josephson energy of the form

$$E = -\text{const}\,\frac{1}{2}(\Psi_1\Psi_2^* + \Psi_1^*\Psi_2) \equiv -E_J\cos\Delta\phi_{12} \tag{9}$$

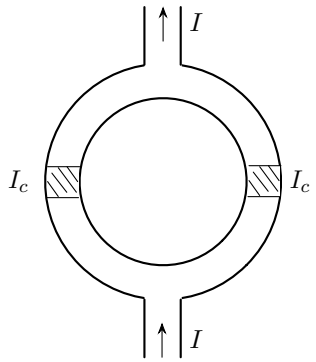
where $\Delta\phi_{12}$ is the (unambiguously defined) phase difference between the coordinates 1 and 2. Except possibly under very special conditions which in practice appear to require ferromagnetic-metal junction[‡] $E_J$ is always positive. A second statement is that if a set of such junctions are inserted in a bulk ring (SQUID geometry) then there is a definite

[‡]Ryazanov et al., PRL **86**, 2427 (2001).

relation between the sum of the phase differences $\Delta\phi_i$ across the various junctions $i$ (taken e.g. 'clockwise' around the ring) and the total flux (external plus self-induced) $\Phi$ trapped through the ring:

$$\sum_i \Delta\phi_i = 2\pi\Phi/\Phi_0 \tag{10}$$

It is an immediate consequence of equations (9) and (10) (and the hypothesis that all $E_J > 0$) that (a) an isolated SQUID ring in zero external field will carry zero current and hence zero trapped flux, irrespective of the number of junctions (and of the self-inductance of the ring), and (b) that in a 'dc SQUID' setup (two junctions with leads attached between them, see figure) the critical current will be modulated by the trapped flux $\Phi$ according to




$$I_c(\Phi) = 2I_c|\cos\pi\Phi/\Phi_0| \tag{11}$$

and this is maximum (zero) for an integral (half-integral) amount of trapped flux. These properties have been repeatedly confirmed experimentally in circuits made entirely out of 'classic' superconductors such as Al or Nb.

Now let's discuss how these considerations are modified when the circuit includes one or more bulk superconductors with an 'exotic' OP. We first have to resolve a 'book-keeping' problem: our definition of the 'amplitude' $\Psi$ of the exotic OP will depend on which lobe we choose as the 'reference' one. It is simplest to resolve this, in the case of a single orientation (e.g., NSEW) of the exotically paired crystal, by arbitrarily choosing a definite direction in absolute space (e.g. 'north') and defining $\Psi$ to be the amplitude of the lobe pointing in this direction.[§]

Josephson experiments on 'exotic' circuits involve two fundamental principles:

(A) If two bulk superconductors, and the interface (junction) between them, are described by a Hamiltonian invariant under the operations of some group $G$, then the Josephson coupling energy must be similarly invariant under $G$.

(B) Equation (10) must hold provided the phase differences $\Delta\phi_i$ are consistently defined relative to one another.

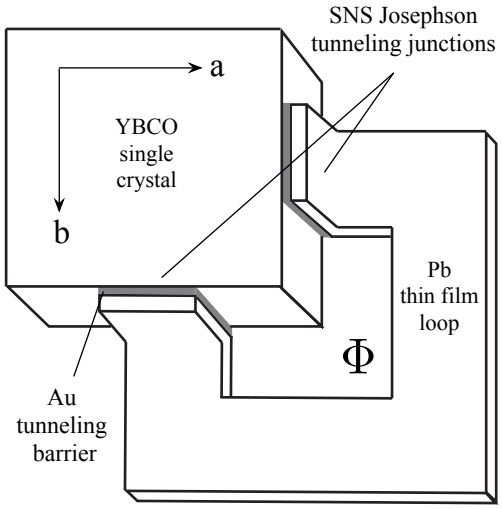
It is convenient to divide existing Josephson experiments into three classes:

(I ) which exploits principle A only,

(II ) which exploits principle B only, and

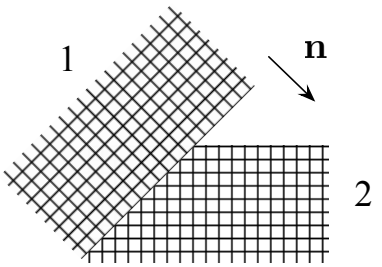
(III) which exploits both A and B.

[§]We implicitly consider for definiteness a $d_{x^2-y^2}$ OP. For the case of $s^-$ or $d_{xy}$ , the definition needs to be modified somewhat, but it is obvious how to do this.



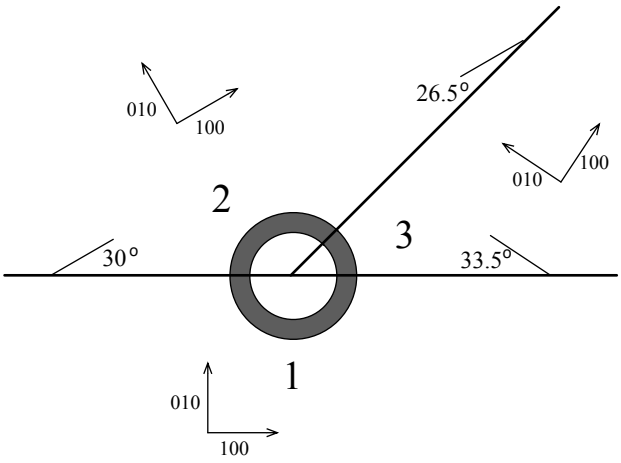

In the following I will assume that we can be confident that any Josephson effects seen in the experiments are lowest-order, i.e., crudely speaking, of the form described by equation (9) (rather than, say, by an energy proportional to $\Psi_1^{*2}\Psi_2^2$); this hypothesis can be (and in many cases has been) checked from the periodicity of the relevant Fraunhofer diffraction pattern.

The importance of principle A is that it often forbids a lowest-order Josephson effect between superconductors of different pairing symmetry (or with the same symmetry but different orientation). The most obvious example is a c-axis-oriented interface between a cubic $s$-wave superconductor 1 (e.g. Pb) and a tetragonal cuprate 2 (e.g. Tl-2201). If the pairing in the cuprate is pure $d_{x^2-y^2}$ and the interface (junction) itself possesses tetragonal symmetry, then invariance of the coupling energy under a $\pi/2$ rotation forbids any lowest-order Josephson coupling, i.e. any expression of the form (9) where $\Psi_2$ is defined as above (since such a rotation preserves the sign of $\Psi_1$ but reverses that of $\Psi_2$). Similarly, an ab-plane junction at 45° between a $d_{x^2-y^2}$-paired superconductor 2 and a second superconductor 1 should show no lowest-order Josephson effect, irrespective of whether 1 has $s$-wave or a $d_{x^2-y^2}$ pairing;[¶] in this case the symmetry involved is reflection in the normal **n** shown. (Again, $\Psi_1$ maintains its sign while $\Psi_2$ is reversed).




The application of principle B is most easily seen from the geometry of the original UIUC experiment (see the figure); for the moment we neglect complications associated with the lack of exact tetragonal symmetry in YBCO. The crucial point is that from symmetry, the coupling of the OP $\Psi_1$ of external $s$-wave OP of Pb to the lobe of the YBCO OP which points normal to the surface must be the same for the two junctions;

[¶]Note however that if 2 is (e.g.) $d_{x^2-y^2}$ and 1 $s^-$ or $d_{xy}$, a lowest-order effect can occur.




thus for example, if we choose our 'reference' lobe (with OP $\Psi_2$) to be vertical, then the vertically oriented (b-axis) junction must correspond to an energy of the form (9), where it is plausible (though not necessary to the argument) that $E_J$ is positive. On the other hand, with this definition the Josephson energy of the horizontally oriented junction must by symmetry be of the form $-E_J \frac{1}{2}(\Psi_1 \tilde{\Psi}_2^* + \text{c.c.})$, where $\tilde{\Psi}_2^*$ is the amplitude of the horizontally oriented lobe. But the vertical and horizontal axes are related by a $\pi/2$ rotation; thus, if the OP YBCO has $s$-wave symmetry ($\hat{R}_{\pi/2} = +1$) we have $\tilde{\Psi}_2 = \Psi_2$, while if it has $d$-wave symmetry ($\hat{R}_{\pi/2} = +1$) the relation is $\tilde{\Psi}_2 = -\Psi_2$. So when the Josephson coupling energy of this junction is expressed in terms of the 'reference' amplitude $\Psi_2$, it is of the form (9) for the $s$-wave case (with $E_J > 0$) but for the $d$-wave case acquires a $-$ sign, i.e., it is $+E_J \cos \Delta\phi_{12}$. It is clear that this phase change of $\pi$ is equivalent to inserting an extra half-quantum of flux into the circuit, so that the SQUID shown in fig. 2 should in the case of $s$-wave pairing, behave 'normally' (maximum critical current at integral values of flux) but for $d$-wave pairing should show the reverse behavior, with maxima at half-integral values of flux and minima at integral (including zero) flux. The original UIUC experiment demonstrated fairly convincingly that the latter result occurs.*

A very elegant circuit design which in some sense exploits both principles A and B is the 'tricrystal-ring' setup of Tsuei and Kirtley: see fig. 3 (all crystals are of identical material) where we should ignore for now all but the central ring. I will discuss a slightly idealized version of this experiment, in which all the angles involved are exactly 30°, and moreover neglect self-inductance effects, so that the equilibrium configuration of the OP's in the various regions is determined by the consideration that the sum of the Josephson couplings across the these interfaces should be a minimum. What does this imply about the quantity $\Delta\Phi_{\text{tot}} \equiv \sum_i \Delta\phi_i$? To put it crudely and intuitively, the 1-2 and 1-3 junctions are related by $\hat{I}_{\text{axis}}$, while the 2-3 and 1-2 junctions are related by $\hat{R}_{\pi/2}$. Thus, if the eigenvalue of $\hat{I}_{\text{axis}}\hat{R}_{\pi/2}$ is $+1$, the configuration which achieves

*For the complications associated with orthorhombicity, lack of exact junction symmetry etc., see section 7 of Annett et al., ref. cit.

minimum total Josephson energy is $\Delta\phi_{\rm tot} = 0$, while if it is $-1$, it corresponds to $\Delta\phi_{\rm tot} = \pi$. These two possibilities for $\Delta_{\rm tot}$ correspond, according to equation (10), to a trapped flux through the hole of zero and half a flux quantum respectively. Since $\hat{I}_{\rm axis}\hat{R}_{\pi/2} \equiv \hat{I}_{45^\circ}$, we see by reference to the Table that observation of zero flux would indicate an $s$ or $d_{xy}$ state, while observation of half a flux quantum would be strong evidence for $s^-$ or $d_{x^2-y^2}$. It should be emphasized that in the absence of more detailed assumptions (in my opinion less firmly based) about the form of the Josephson coupling it is impossible in this geometry to discriminate between the two possibilities in each case. ( However, an experiment[†] similar in concept in a different geometry has ruled out any $s$-wave state, at least in Tl-2201).

There are by now around a couple of dozen quantum phase interference experiments in the literature, of all three types. All type-II experiments to date have been done on YBCO (mostly optimally doped, though a couple are in the underdoped regime) and have indicated that in this system the pairing is $d$-wave, and very probably[‡] $d_{x^2-y^2}$.

All the tricrystal ring experiments[§] have shown that the pairing is either $s^-$ or $d_{x^2-y^2}$; to date these have been done on YBCO, GdBCO, Tl-2201, Bi-2212 and most recently the electron-doped cuprate NCCO. Thus, prime facie, everything is consistent with assignment of a $d_{x^2-y^2}$ OP generically to the cuprates. Unfortunately there is a fly in the ointment: while the type-I experiments concluded to date are generally ambiguous, at least one experiment of this type (Li et al., PRL **83**, 4160 (1999)) has been interpreted by its authors as clearly inconsistent with (pure or majority) $d_{x^2-y^2}$ pairing and evidence rather for a conventional $s$-wave state. I believe however that there are some problems with the geometry of this experiment [discuss], so would take the view that the $d_{x^2-y^2}$ assignment is, at least, substantially more plausible than any alternative.

[†]:Tsuei et al., Nature **387**, 481 (1997).

[‡]Principle A applied to (e.g.) the original UIUC experiment would forbid a $d_{xy}$ states if the YBCO-Pb junctions were invariant under reflection in the normal.

[§]An early type-III experiment in a different geometry ('IBM I') was interpreted as evidence for $s$-wave pairing. See however Annett et al., ref. cit.