Intuitive LCAO band model for $RBa_2Cu_3O_7$ structure

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In honor of Martin Peter's 60th birthday

Abstract. The assumption of a hierarchy of the interactions similar to that in standard *d*-band perovskites and the low *Pmmm* symmetry are shown to result in an intuitive LCAO band model for the idealized $RBa_2Cu_3O_7$ structure and in an apparently new, non-phononic superconducting mechanism in $RBa_2Cu_3O_{7-\delta}$ compounds, which has the merit of featuring a frame fully consistent with the experimental data.

1. Introduction

We would like to contribute to the present Festschrift with a paper joining a few thoughts about work done in common with Professor Martin Peter and some original results the derivation of which makes use of skills obtained while one of us was working under his guidance during the academic year 1974/1975.

In the course of the previous academic year, Professor Martin Peter had started an ambitious research programme devoted to the study of the contribution of the tight binding electrons to the superconducting, elastic and thermodynamic properties of the solids. The first important results have been published at the end of 1974 [1] and then most efforts have been directed towards the unrestricted computation of the superconducting transition temperature of Nb from the Eliashberg equations [2]. During all this effort, Martin Peter was a warm human, a gifted group leader. He did not spare personal efforts and health in the accomplishment of the programme, which he has vigorously pursued during a whole decade. An inherently incomplete survey indicates the existence in this field of fourteen reports with his participation and of 195 citations of these in the literature. The impact of the early references [1] and [2], as seen through the 34 and 49 citations respectively (collected since the date of their publication until the end of 1985), is to be considered important in the worldwide effort of ensuring a sound understanding of the properties of Nb and of its compounds, which, for half a century, had dominated the history of the search for high T_c superconducting materials [3], until the fundamentally new result of Bednorz and Müller [4] had radically changed the course of events.

In retrospect, during our joint effort of deriving an LCAO band model of Nb, two truths have been verified again and again in the investigation of the electronic properties of the solids. First, it is of paramount importance to know from the very beginning which matrix elements, or effects, are the largest and, on the other hand, which of them can be taken as corrections. Second, instead of firmly established hierarchies, important room is often allowed to analogies and plausibility arguments which in the end are required to result in a coherent framework. In what follows, an illustration of their use will be given in the foundation of an as simple as possible LCAO model for the valence and conduction energy bands of the idealized structure RBa$_2$Cu$_3$O$_7$ of the $T_c \sim 90$ K superconducting compounds RBa$_2$Cu$_3$O$_{7-\delta}$, where R stands either for Y [5], or a rare earth (see, e.g., [6–8]), or some specific metallic group [9].

2. Fundamental interactions within RBa$_2$Cu$_3$O$_7$ compounds

The first step towards the derivation of an LCAO model is the knowledge of the crystalline structure of RBa$_2$Cu$_3$O$_7$. Structural data [10, 11, 8, 9] indicate the occurrence of an oxygen-deficient layered perovskite phase, characterized by the symmorphic space group *Pmmm*. Henceforth, when discussing atomic locations within the unit cell, we prefer to keep the notation of the International Tables for X-Ray Crystallography [12]: R($1h$), Ba($2t$), Cu($1a$), Cu($2q$), O($1e$), O($2q$), O($2s$), O($2r$).

Experimental data show the existence of metallic conductivity (see, e.g., [13]) and this in turn is consistent with an electronic band structure one or more bands of which intersect the Fermi surface. Thus, in the study of the electronic properties of RBa$_2$Cu$_3$O$_7$, useful analogy can be made with the cubic perovskites showing band structure [14, chap. 19]. We therefore assume that an LCAO band model would yield good account for the valence and the conduction bands. Always by analogy with standard perovskites, the starting point for a band structure calculation, is the hypothesis that a charge transfer occurs from R, Ba, and Cu to oxygen, such that RBa$_2$Cu$_3$O$_7$ is an ionic crystal.

The occurrence of a distorted perovskite structure has the consequence that it is impossible to ascribe identical states of ionization to all Cu ions within the unit cell. Taking into account that the two Cu($2q$) ions are crystallographically equivalent, it follows that charge neutrality is secured provided they reach Cu^{2+} configuration, while the Cu($1a$) ion reaches Cu^{3+} configuration. Meanwhile, the p shells of the seven O atoms are filled to O^{2-} configurations at the expense of the seven electrons taken from the Cu atoms and of other seven electrons taken from the R atom (which becomes R^{3+}) and the two Ba atoms (which become Ba^{2+}). Similar to the standard perovskites, the role of the R and Ba atoms is essentially terminated at this stage. The properties of the valence and conduction band will be the result of the interactions within the Cu–O sublattice.

Since the interaction of the d states of Cu with states of the neighbouring O ions prevail over the electrostatic interaction between pairs of d electrons located

at a same Cu ion, Hund's rule breaks down and the d-electron structure is to be described by energy bands, within which every state can accommodate two electrons of opposed spins. The independent electron picture therefore holds in the description of the $Cu - d$ electrons in $RBa_2Cu_3O_7$.

Corroborating this result with the conservation of the number of d states as one goes from isolated ions to the band states and with the fact that every d electron preserves to some extent "memory" of its parent ion, three important consequences follow.

3. Three consequences: Jahn–Teller distortion, esr signal, superconducting mechanism in $RBa_2Cu_3O_{7-\delta}$

First, Kramers' theorem [15, Appendix 9] holds true for the d band electrons originating in each Cu^{2+} ion. The direct consequence of the involved spin degeneracy is the Jahn–Teller distortion of the planar $Cu'(q)-O'(s) - O'(r)$ and $Cu''(q) - O''(s) - O''(r)$ configurations: the Cu ions leave the $O(s)-O(r)$ planes and the energy inequivalence of the two sides of these planes quench the Jahn–Teller distortion at $Cu(q)$ locations displaced towards the neighbouring $O(q)$ ions.

Second, the occurrence of a strong Cu^{2+} esr signal and the absence of Cu^{3+} signal [16, 17] is consistent with the abovementioned band arrangement of the d states (with resultant zero spin and hence no signal from Cu^{3+} places and with resultant local $\frac{1}{2}$ spin and hence signal from the Cu^{2+} places).

Third, a non-phononic mechanism of superconductivity seems to emerge naturally from the electron charge distribution and the symmetry of the structure. While each of the two unpaired d electrons is sufficiently well localized around its parent $Cu(q)^{2+}$ ion, in the reciprocal space (where the energy states are counted), Wigner's theorem shows that they have to share the same one-electron energy level, near to the Fermi energy E_F. As a consequence, Cooper pairs arise, one per unit cell of the crystal, with their constituent electrons located respectively within the pairs of parallel quasi-two-dimensional layers $Cu'(q)-O'(s)-O'(r)$ and $Cu''(q)-O''(s)-O''(r)$.

The experiment shows that, in order to stabilize the superconducting phase, the formulas of the compounds have to be modified from $RBa_2Cu_3O_7$ to $RBa_2Cu_3O_{7-\delta}$, $\delta \sim 0.1$, with the oxigen missing at the $O(1e)$ locations [8]. The two $Cu(1a)$ ions located next to an $O(1e)$ vacancy undergo a valence change from Cu^{3+} to Cu^{2+} and this is expected to generate charge instabilities along the $Cu(1a)-O(1e)$ chains. A detailed energy balance should establish how these charge instabilities result in an effective attractive interaction between the pre-existing Cooper pairs in the surrounding quasi-two-dimensional layers.

Whichever the details of the theoretical solution, this mechanism is appealing due to its capability to provide clear meaning to each relevant substructure of $RBa_2Cu_3O_{7-\delta}$. Superconductivity independently follows within every Cu–O

pattern sandwiched in between two nearest R layers. Hence it is quasi-two-dimensional in nature, with, however, an essential role assigned to the Cu(1a)–O(1e) chain length (measured through the oxigen deficiency δ), in agreement with the experimental data. The spin of the R ions is not important. This superconducing mechanism is equally valid for every R species which is trivalent and possesses an ionic radius that accommodates the stoichiometry of the geometric configuration.

4. The LCAO model and analytic results at Γ

In the detailed derivation of the LCAO model, we have closely followed the approach by Harrison for cubic perovskites [14, Chap. 19].

Double counting of the oxigen ions at the unit cell faces is avoided considering only the locations at the $x = a/2$ and $y = b/2$ faces respectively and then supposing that these ions remain invariant under the action of the operators of the *mmm* point group. Then there is no ambiguity in the reduction of the LCAO problem from the entire crystal to a single elementary cell.

In the derivation of the valence and conduction bands, the fifteen $3d$ states of the three Cu ions, the twenty one $2p$ states of the seven oxigen ions *and* the seven $2s$ states of the same oxigen ions are counted. The model therefore includes 43 wavefunctions and results in a 43×43 secular determinant.

As shown by Harrison, due to the symmetry allowed hybridization, the inclusion of the deep lying $2s$ O^{2-} states greatly helps in improving the predictions of the model while keeping the number of independent parameters to a minimum.

Wigner's theorem and the property of the *mmm* point group of being Abelian show that proper characterization of the electron states at Cu(2q), O(2q), O(2s) and O(2r) places is to be made by gerade and ungerade combinations of individual states.

Included in the model are the $sp\sigma$, $pd\sigma$ and $pd\pi$ interactions coming from the pairs of nearest neighbours: Cu(1a)–O(1e), Cu(1a)–O(2q), Cu(2q)–O(2s), Cu(2q)–O(2r), Cu(2q)–O(2q), as well as the $pp\sigma$ and $pp\pi$ interactions coming from the pairs of next nearest neighbours O(1a)–O(2q), O(2s)–O(2r).

The angular dependence of the energy integrals between states in the considered pairs has been derived in the classical paper by Slater and Koster [18]. With the radial dependences established within the pseudopotential theory by Harrison [14, chap. 20], it follows that the model involves a total of eight parameters: at diagonal matrix elements, three one-electron eigenenergies ε_s, ε_p, ε_d, while at off-diagonal matrix elements the intrinsic parameters $\eta_{sd\sigma}$, $\eta_{pd\sigma}$ and $\eta_{pd\pi}$ for nearest neighbours and $\eta_{pp\sigma}^{II}$ and $\eta_{pp\pi}^{II}$ for next nearest neighbours.

These hypotheses are sufficient to develop a simple LCAO model allowing computation of energy levels, densities of state and Fermi surfaces everywhere inside the Brillouin zone.

At lines and points of symmetry of the Brillouin zone, the general 43×43 secular determinant splits into products of lower order determinants according to the irreducible representations of the groups of symmetry characterizing these lines and points. The compatibility relations given, e.g., in the book by Bradley and Cracknell [19] allow correct identification of the results obtained along lines of symmetry with those obtained at points of symmetry. A characteristic feature of the present problem stems from the fact that all the involved symmetry groups are Abelian. Increase in symmetry at the symmetry points is obtained at the expense of the addition of the inversion group $\bar{1}$ as an invariant subgroup and this separates gerade from ungerade states.

As an illustration of the analytic results that can be predicted by the model, let us consider the centre Γ of the Brillouin zone. Here, the secular determinants associated to the eight existing irreducible representations $\Gamma_i^+, \Gamma_i^-, i = 1, \ldots, 4$, have respectively the orders 11, 5, 2, 5, 1, 5, 9, 5.

Except for Γ_3^+ and Γ_1^-, there is no fully analytic solution of the involved secular equations. Nevertheless, the gross features of the energy band spectrum can be obtained provided notice is taken of the following facts: the orthorhombic distortion from tetragonal is small; the $Cu(2q)$ Jahn–Teller distortion is small enough to admit to first approximation that the $Cu(2q)$ ions lie within the $O(2s)$–$O(2r)$ planes; the interatomic distances within the pairs $Cu(1a)$–$O(2q)$ are roughly the same as those within the pairs $Cu(1a)$–$O(1e)$, $Cu(2q)$–$O(2s)$, $Cu(2q)$–$O(2r)$ and the same is respectively true for the next nearest neighbour pairs. There result then three distinct energy integrals only among the pairs of next neighbours: $V_{sd\sigma}, V_{pd\sigma}, V_{pd\pi}$. Similarly, the next nearest neighbour interactions can be characterized by two energy integrals, $E_{xx} = (V_{pp\sigma}^{II} + V_{pp\pi}^{II})/2$ and $F_{xx} = V_{pp\pi}^{II}$. For the remaining $Cu(2q)$–$O(2q)$ pairs, pseudopotential theory shows that the energy integrals are about one third from the values $V_{sd\sigma}, V_{pd\sigma}$, and $V_{pd\pi}$ respectively.

Another important step towards the derivation of an analytic solution at Γ consists in the definition of *directional bonding states* within every irreducible representation. For the four ion set $\{O'(s), O''(s), O'(r), O''(r)\}$, these are obtained as even and odd combinations respectively within each of the gerade and ungerade manifolds of s states and of p_α states. For the pair $\{O'(q), O''(q)\}$, "ghost" sp_α states are defined following Harrison [14, Sec. 19.5], by exploitation of the property of the parameters $\eta_{sd\sigma}$ and $\eta_{pd\sigma}$ of being nearly equal.

Under these assumptions, every secular determinant has been got block (quasi)diagonalized into 2×2 or 3×3 pieces for every irreducible representation and it has been possible to get analytic solution to every energy (sometimes by use of perturbation theory).

Similar to the cubic perovskites, while the relative displacement of the $2s$ states due to hybridization has been found to be small, this has been found to be important for the $2p$ and the $3d$ states. In cubic perovskites, however, there occur $s - d$ hybridization only, whereas the oxigen p states are completely decoupled at Γ. By contrast, in the present structure, the $O'(q)$–$O''(q)$ pair states are involved in important $s - p - d$ or $p - d$ hybridizations. Within the gerade representations

Γ_i^+, there are Cu(1*a*) states which are involved in these hybridizations as follows:

Γ_1^+: the two ghost sp_z states with $d_{3z^2-r^2}$
Γ_2^+: the ungerade p_x with d_{xz}
Γ_4^+: the ungerade p_y with d_{yz}.

Within the ungerade representations Γ_i^-, there are involved, besides $O'(q)-O''(q)$ states, O(1*e*) states and ungerade $Cu'(q)-Cu''(q)$ as follows:

Γ_2^-: p_y of O(1*e*), gerade p_y of $O'(q)-O''(q)$
and ungerade d_{yz}
Γ_4^-: the similar p_x, gerade p_x and ungerade d_{xz} states.

As a rule, the eight abovementioned energy parameters of the model are to be found from band fitting to exact results yielded by more expensive methods. In the absence of such data, numerical values have been borrowed from the book by Harrison [14]. Using the structure data values reported in Ref. 11, it has been possible to get an independent numerical evaluation of the spectrum at Γ. In spite of the fact that the energy parameters have not been fit values, a qualitative agreement has been obtained with the energy levels found by Freeman et al. [20] by means of sophisticated computation.

This is an encouraging result. It shows that the pair of $O'(s)-O'(r)$, $O''(s)-O''(r)$ layers as a whole defines the electronic properties (through the *s* and *p* four state combinations with directional bonding). Taking into account the symmetry-induced mixing of the *d* states of the $Cu'(q)$ and $Cu''(q)$ ions in a same elementary cell as well, it results that a consistent theoretical model of superconductivity in $RBa_2Cu_3O_{7-\delta}$ compounds cannot separate the quasi-two-dimensional layers $Cu'(q)-O'(s)-O'(r)$ and $Cu''(q)-O''(s)-O''(r)$ from each other. Moreover, the remarkable participation of the O(2*q*) ions to the eigenstate hybridization is consistent with a distinct role of these cross-ties in the chain-layers interaction.

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