Spontaneous symmetry breaking approach to La$_2$CuO$_4$ properties: hints for matching the Mott and Slater pictures

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Special solutions of the Hartree-Fock (HF) problem for Coulomb interacting electrons, being described by a simple model of the Cu-O planes in La$_2$CuO$_4$, are presented. One of the mean field states obtained, is able to predict some of the basic properties of this material, such as its insulator character and the antiferromagnetic order. The natural appearance of pseudogaps in some states of this compound is also indicated by another of the HF states obtained. These surprising results follow after eliminating spin and crystal symmetry restrictions which are usually imposed on the single particle HF orbitals, by means of employing a rotational invariant formulation of the HF scheme which was originally introduced by Dirac. Therefore, it is exemplified how, up to now being considered strong correlation effects, can be described by improving the HF solution of the physical systems. In other words, defining the correlation effects as such ones shown by the physical system and which are not predicted by the best HF (lowest energy) solution, allows to explain currently assumed as strong correlation properties, as simple mean field ones. The discussion also helps to clarify the role of the antiferromagnetism and pseudogaps in the physics of the HTSC materials and indicates a promising way to start conciliating the Mott and Slater pictures for the description of the transition metal oxides and other strongly correlated electron systems.

PACS numbers: 71.10.Fd,71.15.Mb,71.27.+a,71.30.+h,74.20.-z,74.25.Ha, 74.25.Jb,74.72.-h

The Hubbard models in the theory of strongly correlated electron systems are notably successful [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. They remarkable reproduce the properties of Mott insulators, such as metal-transitions oxides and copper-oxygen layered HTc compounds [2]. However, the search for approaches having more basic foundations do not cease, hoping that they could open the way for obtaining more exact and specific results [11]. The so called first principle or Slater procedures, are electronic structure calculations that begin by considering the interactions among electrons or atoms in vacuum. The study of the band structure they predict, in principle should offer a way for the precise determination of the physical properties of each material [11, 12, 13]. However, the above mentioned potentialities had been falling in describing many systems showing strong correlation effects [7].

The motivation of the present letter emerged from a suspicion that the Hartree Fock (HF) method, could had been underestimated in its possibilities for helping in clarifying the above mentioned difficulties [2, 14]. As a net result of this work, we came to believe that a large deal of correlation effects, can be described in the framework of the HF scheme, after removing certain symmetry restrictions which obstacle the finding of the best HF solutions. By example, it has been early shown by Slater in Ref. [2], that sometimes the HF potential breaks the symmetry of the original crystalline lattice, creating magnetic structures and gaps. This symmetry breaking effect has been also more recently underlined and deepened in Ref. [16]. However, the removal of the lattice symmetry restrictions alone had not been able to describe the insulator properties of a large class of materials [1, 2, 11]. One of the central results of the present investigation, is the identification of another kind of symmetry restriction that seemingly had been overlooked for a long time. It corresponds to the usual assumption about the necessary $\alpha (S_z = 1/2)$ or $\beta (S_z = -1/2)$ orientations of the spin of each solution for the HF orbitals [12, 17]. For supporting this main statement, the work considered the HF problem as applied to a simple one band model of the superconducting material La$_2$CuO$_4$, looking from the start for single particle orbitals being non separable in their spacial and spinor dependence. That is, they will have the structure $\phi(x, s) \neq \phi(x)\psi(s)$, i.e. the orbitals have not an absolute common quantization direction for their electron spin. Note, that to proceed in this way means not other thing that to apply the Dirac’s formulation of the HF procedure [14]. The results, as it will be seen, are able to describe the basic properties of the La$_2$CuO$_4$ [13]. We would like to stress that the obtained results do not look so radical if we consider the following circumstance: the correlation effects are associated with the difference shown by the system’s properties with the ones predicted by the HF procedure applied to it. Therefore, what we have argued here, is simply that the there exist unexplored improvements of the mean field schemes which allow to predict properties which are currently considered as strong correlation properties. These modifications of the HF method are related with usual constraint which are imposed on the crystalline and spin properties of the single particle orbitals. The possibility of their employment for solving the long standing debate between the Slater and Mott pictures in the theory of transition metal oxides and HTc
superconducting materials will be considered elsewhere.

In this letter, we will firstly describe the physical basis of the model employed and after that, the results obtained for the various HF solutions will be presented. For the details of the concrete solutions we refer to the extended version of this work in Ref. [18].

Let \( \mathcal{H}(x_1, \ldots, x_N) = \sum_i \mathcal{H}_0(x_i) + \frac{1}{2} \sum_{i \neq j} V(x_i, x_j) \), be the N-electrons system hamiltonian, including kinetic plus interaction with the environment hamiltonian \( \mathcal{H}_0 \), besides Coulomb interaction among pairs of electrons \( V \). The HF equations of motion were solved by allowing for nonseparable solutions for the orbitals \( \phi_\eta(x, s) \), where \( \eta = k_1, \ldots, k_N \) are the labels of the HF basis they form. The system of HF equations is rotational invariant when formulated in the general HF procedure firstly introduced by Dirac in Ref. [14]. Its explicit expression for the here considered problem can be found in Refs. [14, 18].

Let us first present the effective band model used to describe the dynamic of the less bounded electrons in La\(_2\)CuO\(_4\). It is known that at low temperature La\(_2\)CuO\(_4\) is an antiferromagnetic-insulator [15]. However, in evident contradiction with the experiments the Linear Augmented Plane Waves (LAPW) band calculations predicts for it metal and paramagnetic zero temperature properties [12]. Nevertheless, such band studies results at least show that the conduction electrons are strongly coupled to the Bravais lattice centers of the copper oxygen planes. Clearly this tight-binding behavior is determined by the interaction of the electrons with its surrounding effective environment. The less bounded electron in the La\(_2\)CuO\(_4\) molecule is the Cu\(^{2+}\)'s not paired one. At difference from O\(^{2-}\) ions, Cu ones do not have their last shell (3d) closed. Those copper 3d electrons partially fill the last band of La\(_2\)CuO\(_4\) solid in and what follows they shall be referred as: the electron gas. It seems appropriate to consider those electrons as strongly linked to CuO\(_2\) cells and with special preference for the Cu centers [5]. Thus, our Bravais lattice is going to be the squared net \((x, y)\) with special preference for the Cu centers [5]. Thu s, our Bravais lattice is going to be the squared net (see figure 1). Further, the presence of electrons pertaining to the various fully filled bands in the model plus the nuclear charges, will play a double role in the model. Firstly, they will act as an effective polarizable environment screening the field of the charges in the electron gas. It will be reflected by a dielectric constant \( \varepsilon \) reducing the Coulomb interaction. Secondly, the mean field created by the environment will act as a periodic potential \( W_{\gamma} \), tight-binding the electrons to the Cu centers. The interaction \( F_b \) among the electron gas and a "jellium" neutralizing its charges is also considered. It was be modeled as a gaussian distribution of positive charges \( \rho_b(y) = \frac{1}{4\pi}\varepsilon\varepsilon_0 \exp(-\frac{y^2}{b^2}) \), surrounding each lattice point and having a characteristic radius \( b \). In resume, the free hamiltonian of the model takes the form

\[
\mathcal{H}_0(x) = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + W_{\gamma}(x) + F_b(x),
\]

where \( \hat{p}_i^2 \) is the i-th electron’s squared momentum operator; \( m \) is the electron mass; \( \varepsilon_0 \) is the vacuum permittivity and lattice vectors \( \mathbf{R} = n_1 \mathbf{e}_x + n_2 \mathbf{e}_y + n_3 \mathbf{e}_z \) with \( n_1, n_2, n_3 \) being integers, move on Bravais lattice. It will be referred in what follows as the the absolute lattice. The versors \( \mathbf{e}_x \) and \( \mathbf{e}_z \) are resting on the direction defined by the lattice’s nearest neighbors (see figure 1a)). The distance between Cu nearest neighbours is \( \approx 3.8 \text{ Å} \). The interaction among pairs of electrons is taken in the form \( V(x, y) = \frac{e^2}{4\pi\varepsilon\varepsilon_0 |x-y|} \), which includes the dielectric constant associated to the presence of the effective environment.

We are seeking here for HF solutions with orbitals having a non separable spin and orbit structures. Thus, it was considered that the spin can show a different projection for the different Wannier orbitals to be superposed for defining those orbitals. The spin for each of them will be either or \( \alpha \) or \( \beta \) type, according they are linked either to one or the other of the two sublattices shown in figure 1a)). The points of these sublattices were defined as follows: \( \mathbf{R}^{(r)} = \sqrt{2}n_1 \mathbf{q}_1 + \sqrt{2}n_2 \mathbf{q}_2 + \mathbf{q}^{(r)}, r = 1, 2; \) with \( n_1 \) and \( n_2 \) \( \in \mathbb{Z} \), and in which the vector \( \mathbf{q}^{(r)} = 0 \) if \( r = 1 \) and \( \mathbf{q}^{(r)} = \mathbf{p} \mathbf{e}_z \) when \( r = 2 \); and where \( \mathbf{q}_1 \) and \( \mathbf{q}_2 \) form the basis versors on each one of them. The searched solutions were constructed as eigenfunctions of the operators \( \hat{T}_{\mathbf{R}^{(r)}} \) belonging to the translation group transforming each sublattice on itself: \( \hat{T}_{\mathbf{R}^{(r)}} \phi_{\mathbf{k},l} = \exp(i \mathbf{k} \cdot \mathbf{R}^{(r)}) \phi_{\mathbf{k},l} \). Therefore we imposed periodic boundary conditions on the \( \phi_{\mathbf{k},l} \) in the absolute lattice’s boundaries \( x_1 = -p \mathbf{L} \) and \( p \mathbf{L} \), \( x_2 = -p \mathbf{L} \) and \( p \mathbf{L} \) (see figure 1a)). This condition determines the allowed set of quasimomenta \( \mathbf{k} = \frac{2\pi}{L}(n_1 \mathbf{e}_x + n_2 \mathbf{e}_y), \) with \( n_1, n_2 \in \mathbb{Z} \) and \( -\frac{L}{2} < n_1, n_2 < \frac{L}{2} \). Note that we are demanding less than the full crystal symmetry on the single particle states which we are looking for. Let
FIG. 1: The figures show: a) The point lattice associated to the Cu-O planes. For removing the symmetry restrictions, it will be helpful to separate the lattice in the two represented sublattices; and b) shows the corresponding base of the Cu-O planes.

the single particle states represented in the explicitly non separable form

\[ \phi_{k,l}(x,s) = \sum_{r,\sigma_z} D_{r,\sigma_z}^{k,l} \phi_{r,\sigma_z}^{(r,\sigma_z)}(x,s), \]

where \( l \) is the additional label needed for indexing the stationary states. The tight binding Bloch basis \( \phi_{r,\sigma_z}^{(r,\sigma_z)} \) appearing is defined as

\[ \phi_{r,\sigma_z}^{(r,\sigma_z)}(x,s) = \sqrt{\frac{2}{N}} u^{\sigma_z}(s) \sum_{R^{(r)}} \exp(i \cdot \mathbf{k} \cdot \mathbf{R}^{(r)}) \varphi_{R^{(r)}}(x), \]

\[ \hat{\sigma}_z u^{\sigma_z} = \sigma_z u^{\sigma_z}, \]

\[ \varphi_{R^{(r)}}(x) = \frac{1}{\sqrt{\pi a^2}} \exp(-\frac{(x-R^{(r)})^2}{2a^2}), \quad a \ll p, \]

where \( N \) is the number of electrons in the electron gas, \( \hat{\sigma}_z \) is the spin \( z \) projection operator, where \( z \) is the orthogonal direction to the copper oxygen CuO\(_2\) planes; \( \sigma_z = -1, 1 \), are the eigenvalue of the previously mentioned operator and \( r = 1, 2 \), is the label which indicates each one of the sublattices. As we are working at half filling condition, then \( N \) is equal to the number of cells in the periodicity region \( N_c \). Note that in his simple model, the electron were considered as moving in two dimensions and that gaussian T.B. Wannier orbitals had been assumed \[18\].

FIG. 2: The figure 1 a) shows the Brillouin zone associated the absolute lattice. The grey region signals the Brillouin zone (B.Z.)of the sublattices. The unit of quasimomentum is \( \frac{\pi}{p} \). Figure b) shows the doubly degenerated bands associated to a paramagnetic and metallic state. The zero energy level in all the band diagrams is the Fermi energy of the isolator and antiferromagnetic solution.

The first solution considered, to be called the PM one, was one having their orbitals being eigenfunction of the maximal group of translations leaving invariant the absolute lattice. That is, the maximum possible crystal symmetry is demanded. Also, the spin structure of the orbitals were assumed to be of \( \alpha \) or \( \beta \) types. For this case, figure\[2\] shows the paramagnetic, metallic and doubly degenerate band obtained from an iterative process of solving the HF equation in Ref. \[18\]. For the case of \( N = 20 \times 20 \) electrons, the momenta of occupied states are shown in figure\[2\]a). They lay inside the shadowed square of side \( \sqrt{2\pi}/p \) the Brillouin zone (B.Z) of the sublattices. The condition of reproducing
the bandwidth of 3.8 eV for the conduction band reported in Ref. [12], allowed to fix the dimensionless values of
the free parameters of our model to be: $\epsilon=10$, $\tilde{a}=0.25$, $\tilde{b}=0.05$ and $\tilde{\gamma}=-0.03$. See Ref. [12]
for those dimensionless definitions. The here obtained band topologically coincides with the conduction band result of Ref. [12].

After being determined the parameters of the model, we searched for general HF solutions showing a non separable
structure, and moreover, also retaining a reduced translational symmetry in the defined sublattices. The iterative
process employed for finding this solution, started from a particular state having an antiferromagnetic character from
the beginning (see Ref. [18]). This initial form helped the convergence toward the results being depicted in figure 3.
It shows two sets of bands following for a half filling band, associated to two periodicity lattices having 20x20 and
30x30 cells. The difference between the energies in them is of the order of $10^{-5}$ dimensionless units of energy $\hbar^2/m\sigma^2=8.3$ eV. The measure of the gap shown indicate that the bands correspond to insulating states. The close similarity
between both results indicates that the thermodynamical limit has been achieved. The HF energy of this solution
was the lowest among of all the ones found. It also follows that in coincidence with the experimental evidence, these
states show a local magnetic moment resting on the direction of the sublattice $x_{12}$ as shown in figure 4. In the figure 4 a) the only non vanishing component of the magnetization $m$ in this solution is plotted. An interesting result
is that it has been experimentally observed that $\text{La}_2\text{CuO}_4$ has a magnetic moment of 0.68 $\mu_B$ per Cu site on the
CuO plane [15], and the value obtained from evaluating the magnetization of this HF state turns out to be 0.67 $\mu_B$.
Therefore, the considered here discussion satisfactorily predicts the whole antiferromagnetic structure of $\text{La}_2\text{CuO}_4$.
The antiferromagnetic and isolator solution will be referred below as the IAF state. The single particle states of

![FIG. 3: Energy bands obtained for: a) A sample of 20x20 cells, $E_{gap} = 1.32$ eV. b) A sample of 30x30 cells, $E_{gap} = 1.32$ eV. The zero energy level is chosen in the Fermi level of the 20x20 system and the plotting region is the B.Z. of the sublattices: the shadowed square of side $\sqrt{2}\pi/p$ in Fig. 2 a).](image)

![FIG. 4: The magnetization vector $m$ of the more stable HF state rests in the direction 1-2. a) The figure shows the projection $\tilde{m}_{12}$ of the dimensionless magnetization, in the 1-2 direction. The magnetization unit is $\mu_B$. b) The picture shows a scheme of the mean magnetic moment per site in the lattice. The figure insertion below depicts the angle between the magnetization components of each orbital on each of the sublattices. Note that the orbitals are more AF like as they become close to the Fermi level. The plotting area is again the B.Z. of the sublattices shown in Fig. 2 a).](image)

this solution carry a more intensive antiferromagnetism as more closer they are in energy from the Fermi surface.
This property offers a clear explanation of the gradual loss observed in the antiferromagnetic order under the doping
with holes [3]. The dependence of the angle $\phi$ between the magnetic moments per cell on each of the two sublattice
shown by a given Bloch orbital, is plotted in the insertion at the bottom of figure 4. These components are defined
as the integrals of the magnetic moment over all the unit cells of the *absolute* lattice centered in the sublattice points \[18\]. Then, this HF solution indicates that after the orbitals are allowed to spatial dependent spin orientations, the electrons prefer to reorient their spin when traveling between contiguous lattice cells. Note that the states laying just on the Fermi surface are perfectly antiferromagnetic ones, and that the more away from the boundaries the orbitals are, the less antiferromagnetic they become. Further, in figure 5 a) the band spectra corresponding to another HF paramagnetic ground state (to be named as the PPG one), obtained from the HF equations in Ref. \[18\] is shown. This solution was obtained by only requiring the orbitals to show the full translational symmetry of the CuO planes but not an \( \alpha \) or \( \beta \) type of their spin structure. Note that simply allowing this last freedom determined the existence of a pseudogap in the state. It reaches a maximum value of 0.1 eV \( \approx 10^3 \text{K} \) (equivalent to 0.012 dimensionless unit of energy \( \hbar^2/ma^2 = 8.3 \text{eV} \)). It is an interesting outcome that the HF energy of this ground state is exactly coincident with the one corresponding to the paramagnetic and metallic state. Moreover, the occupied single particle states in both solutions are identical and in consequence the momentum dependence of the filled energy bands also coincide. Henceforth, the difference between the two solutions only refers to the non occupied states. It thus follow that the HF energies per particle of the paramagnetic-metallic (PM), and the paramagnetic with pseudogap (PPG) HF states coincide. They show a value +0.076 eV higher than the energy per particle corresponding to the insulator-antiferromagnetic (IAF) ground state. The spin structure of the excited states can be seen as a dynamical "correlation" effect determined by the freedom allowed to the HF orbitals. It is worth noticing that the energy difference PM (PPG)-IAF and the N´eel temperature of this kind of materials are both of the order of \( 10^2 \text{K} \). Then, the results suggest the possibility of having further success in applying the approach started in this work to the description of some regions of the phase diagram of the La\(_2\)CuO\(_4\). In Figure 5 b) the PPG (PM) and IAF occupied bands are depicted in a common frame. The main difference in their energies corresponds to the single particle states being closer to Fermi surface. As noted before the same behavior has the antiferromagnetic character of the single particle states of the IAF solution. Therefore, it is suggested that both solutions could evolve toward a common ground state lacking an absolute magnetic order under doping with holes. This indication is in correspondence with the pattern shown by the phase diagrams of these materials \[15\].

We express our gratitude to A. González, C. Rodríguez, A. Delgado, Y. Vázquez-Ponce and N. G. Cabo-Bizet by helpful conversations and comments. In addition, the relevant support received from the Proyecto Nacional de Ciencias Básicas (PNCB, CITMA, Cuba) and from the Network N-35 of the Office of External Activities (OEA) of the ASICTP (Italy) are deeply acknowledged.

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[1] N. F. Mott, Proc. Phys. Soc. A62, 416, (1949).
[2] J. C. Slater, Phys. Rev. 81, 385, (1951).
[3] R. Peierls, Proc. Phys. Soc. A49, 72 (1937).
[4] F. Hubbard, Proc. R. Soc. A276, 238 (1963).
[5] P. W. Anderson, Science 235, 1196, (1987).
[6] W. Kohn, Phys. Rev. A171, 133 (1964).
[7] M. Imada, Rev. Mod. Phys. 70, 4 (1998).
[8] E. Dagotto, Rev. Mod. Phys. 66, 763 (1994).
[9] Y. Yanase, Phys. Rep. 387, 1 (2003).
[10] A. Damascelli, Rev. Mod. Phys. 75, (2003).
[11] K. Terakura, A. R. Williams, T. Oguchi and J. Kubler, Phys. Rev. Lett. 52, 1830 (1984).
[12] L. F. Mattheiss, Phys. Rev. Lett. 58, 1028 (1987).
[13] W. Kohn and L. J. Sham, Phys. Rev. A140, 1133 (1965).
[14] P. A. M. Dirac, Proc. Cambridge. Phil. Soc. 26, 376 (1930).
[15] W. E. Pickett, Rev. Mod. Phys. 61, 2 (1999).
[16] C. Yannouleas and U. Landman, Phys. Rev. Lett. 82, 5325 (1999).
[17] A. Szabo and N. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, Dover Publications Inc., Mineola, New York (1989).
[18] A. Cabo-Bizet and A. Cabo Montes de Oca, cond-mat [arXiv:0810.1350] (2008), to be submitted.