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BACHELOR THESIS

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Entanglement in the electronic structure of CuO

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Memento audere semper.
Cuprates are interesting materials composed by copper-oxygen atoms layers that become superconductive at high temperatures. In particular they show superconductive properties when two electrons are removed from the layers (charge $+2$). In this work we want to study the quantum correlation, i.e. entanglement, that subsists between these holes and see how it changes in function of the energy gap, defined as the energy needed to remove an electron from the first ionization state. Our starting point will be a matrix of all possible states obtained by a fitting process of the photoemission spectrum of the second electron. We will consider each state independently and compute entanglement using the Von-Neumann entropy of the reduced state. We will then discuss the projections of states on 3 different orbitals and their charge, pointing out the fact the for high charged states we have low values of entanglement, especially when the $E_{\text{gap}}$ is low.
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Quantum entanglement is a physical phenomenon which occurs when pairs or groups of particles interact in ways such that the quantum state of each particle cannot be described independently of the state of the other, even when the particles are separated in space [4]. The goal of this work is to study how entanglement changes in function of the energy gap inside a specific cuprate, containing CuO layers composed by a copper atom in the middle surrounded by 4 atoms of oxygen. Cuprates are interesting materials because, when doped, they show superconductor properties at high temperatures ($T_c = 134\, K$).

Two electrons (or two holes) in a CuO layer composed by a C atom in the middle with four O atoms around it, repel each other due to a strong Coulomb interaction. The strength of this repulsion—known as the correlation energy—depends on whether the electrons or holes are located on copper or oxygen atoms. This could ultimately determine the superconducting behavior of the charge carriers [2]. Understanding the quantum correlations between these missing electrons (holes) could help us learning more about superconductivity. Our starting point is a block matrix obtained from the study of the photoemission spectrum of the second electron of the CuO$^{2-}$ layer, describing all possible 59 two holes states.

In Chapter 1 we recall the most important concepts of quantum mechanics and explain the formalism of density matrices and tensor products introducing the measure for entanglement. We then describe how to compute entanglement through the Schmidt decomposition and Von-Neumann entropy of the reduced state. In chapter 2 we focus on the physical system of CuO, describing the main properties and structure of these particular layer.

Finally, in Chapter 3 we gather states in different symmetry classes and analyze how entanglement changes in function of the $E_{\text{gap}}$ (i.e. energy gap), showing that there are classes whose states’ entanglement is hardly affected by $E_{\text{gap}}$. We then discuss how entanglement is correlated to the charge, especially in the case of a low $E_{\text{gap}}$ and only for those states that have a high component in the orbital described by both holes on the oxygen atoms. We propose a starting point for a future research, pointing out the fact that a study for lower $E_{\text{gap}}$ could evidence a deeper correlation between charge and entanglement.
1. Entanglement

Entanglement is a quantum phenomenon in which the states of two or more objects can not be described separately, even though the individual objects may be spatially divided.

To begin with, we want to give a definition of a Hilbert space, since every physical quantum state can be associated with a vector in a specific Hilbert space. We then introduce the concepts of observables, operators and density matrices. We proceed with the description of bipartite states and entanglement and finally we introduce the Von-Neumann entropy of the reduced state as a measure of entanglement [8][4].

1.1 Hilbert spaces

A Hilbert space $H$ is a real or complex inner product space that is also a complete metric space with respect to the distance function induced by the inner product. In this work we will deal with Hilbert spaces of finite dimensions. For example, if we are dealing with the spin of an electron (that can only be up or down), we will have a Hilbert space of dimension 2.

1.1.1 Properties of Hilbert spaces

In the braket formalism the ket $|\phi\rangle$ denotes an element of $H$. As stated above $H$ is a complex vector space on which there is an inner product $\langle x|y \rangle$ associating a complex number to each pair of element $x, y \in H$ that satisfies the following properties:

1. The inner product of a pair of elements is equal to the complex conjugate of the inner product of the elements

\[
\langle x|y \rangle = \langle \bar{y}|\bar{x}\rangle
\]

where $\langle x|$ is the dual of the ket $|y\rangle$ and is called bra.

2. The inner product is linear in its first argument. \(\forall a, b \in \mathbb{C}\)

\[
\langle ax_1 + bx_2|y \rangle = \langle ax_1|y \rangle + \langle bx_2|y \rangle
\]

3. The inner product of an element with itself is positive definite:

\[
\langle x|x \rangle \geq 0
\]
In particular, we have
\((|\psi\rangle)\dagger = \langle \psi |\) \hfill (1.4)
and vice versa. For each ket we associate its dual bra, with a 1-to-1 correspondence.

The norm of a vector is defined as \(||\psi||^2 = \langle \psi |\psi \rangle\). Each state \(|\psi\rangle\) can be written as a linear superposition of the orthonormal basis states \(|n\rangle\) (such that \(\langle m|n \rangle = \delta_{nm}\)) of \(\mathcal{H}\)
\[|\psi\rangle = \sum_n c_n |n\rangle \quad c_n = \langle \psi |n \rangle\] \hfill (1.5)
Moreover, if \(|x\rangle, |y\rangle \in \mathcal{H}\) the condition of orthonormality is expressed as \(\langle x |y \rangle = \delta_{xy}\), where \(\delta_{xy}\) is the Kronecker delta.

1.1.2 Operators and observables

In quantum mechanics, observable quantities such as the position, spin or energy of a particle are described by operators acting on \(\mathcal{H}\). In order to be an observable, an operator \(\hat{A}\) must be Hermitian, i.e. selfadjoint (\(\hat{A} = \hat{A}^\dagger\)). Applying an operator to a generic state \(\psi\) sends the initial state to another state
\[\hat{A} |\psi\rangle = |\phi\rangle\] \hfill (1.6)
If \(\hat{A}\) is Hermitian, the spectral theorem ([8]) states that there exists a set of states \(|a_n\rangle\) (i.e. eigenvectors) and a set of real numbers \(a_n\) (i.e. eigenvalues) such that
\[\hat{A} |a_n\rangle = a_n |a_n\rangle\] \hfill (1.7)
If \(|a_n\rangle\) and \(|a_m\rangle\) are both eigenvectors of \(\hat{A}\), they satisfy the orthonormal condition \(\langle a_n |a_m \rangle = \delta_{mn}\). Using the spectral decomposition of an operator, we can write it as
\[\hat{A} = \sum_n a_n |a_n\rangle \langle a_n|\] \hfill (1.8)
where \(|a_n\rangle \langle a_n|\) denotes the outer product between \(|a_n\rangle\) and \(|a_n\rangle\).

A special type of operators are the projection operators \(\hat{P}\) defined as \(P^2 = P\); the projection on \(|\psi\rangle\) is then given by
\[\hat{P}_\psi = |\psi\rangle \langle \psi|\] \hfill (1.9)

We can now introduce the meaning of ”measurement”. In quantum mechanics the outcomes of a measurement are given by the eigenvalues \(a_n\) of the corresponding observable \(\hat{A}\).
Let us consider the system in the state $|\psi\rangle$. The probability to measure $a_n$ is

$$p(a_n) = |\langle \psi | a_n \rangle|^2$$  \hspace{1cm} (1.10)$$

and, since $p(a_n)$ is a real number between 0 and 1, we also have that

$$\sum_n |\langle \psi | a_n \rangle|^2 = 1$$  \hspace{1cm} (1.11)$$

Thus, if $|\psi\rangle = |a_n\rangle$, that is if $|\psi\rangle$ is an eigenvector of $\hat{A}$, we will measure the eigenvalue $a_n$ with probability 1. The average value of an observable $\hat{A}$ is then the weighted sum of all its eigenvalues and can be written as

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \sum_n a_n |\langle \psi | a_n \rangle|^2$$  \hspace{1cm} (1.12)$$

It also happens that whenever we make a measurement of an observable $\hat{A}$ of a state $|\psi\rangle$, the state will always collapse into the eigenvector $|a_n\rangle$ of $\hat{A}$ with eigenvalue $a_n$.

For example, suppose we want to measure the spin $\hat{S}$ of an electron whose initial state $|\phi\rangle$ is a superposition of the two eigenvectors $|\pm\rangle$ of $\hat{S}$ with eigenvalues $\pm \hbar/2$. When we apply $\hat{S}$ to $|\phi\rangle$, only two possible outcomes are possible.

$$\hat{S} |\phi\rangle = \hbar/2 |+\rangle \quad \text{or} \quad \hat{S} |\phi\rangle = -\hbar/2 |-\rangle$$  \hspace{1cm} (1.13)$$

### 1.2 Entangled states

In section 1.1 we discussed how to describe a single quantum state such as a single electron or photon. We now want to introduce bipartite states, i.e. quantum states consisting of two subsystem described by the tensor product of different Hilbert spaces, and define the difference between separable and entangled states.

#### 1.2.1 Tensor product of two vector spaces

Let us construct the space of states of two physical independent systems. Let $\mathcal{H}_1^N$ and $\mathcal{H}_2^M$, of dimensions N and M respectively, be the spaces of states of the two systems and let $|\phi\rangle \in \mathcal{H}_1^N$ and $|\psi\rangle \in \mathcal{H}_2^M$. The pair $|\psi\rangle, |\phi\rangle$ can be viewed as a vector belonging to a Hilbert space of dimension NM, called tensor product of $\mathcal{H}_1^N$ and $\mathcal{H}_2^M$, denoted as $\mathcal{H}_1^N \otimes \mathcal{H}_2^M = \mathcal{H}_{12}^{MN}$.

Given an orthonormal basis $|n\rangle$ for $\mathcal{H}_1^N$ and $|m\rangle$ for $\mathcal{H}_2^M$, we can write

$$|\phi\rangle = \sum_{n=1} \alpha_n |n\rangle, |\psi\rangle = \sum_{m=1} \beta_m |m\rangle$$  \hspace{1cm} (1.14)$$

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The tensor product between $|\phi\rangle$ and $|\psi\rangle$ is then defined as

$$ |\phi \otimes \psi\rangle = \sum_{n,m} c_n d_m |n \otimes m\rangle \quad (1.15) $$

This is true whenever the two systems are independent. The most general state vector $|\chi\rangle \in \mathcal{H}$ will be of the form

$$ |\chi\rangle = \sum_{n,m} b_{nm} |n \otimes m\rangle \quad (1.16) $$

where $|n \otimes m\rangle$ is the tensor product between $|n\rangle$ and $|m\rangle$ and $b_{nm} \in \mathbb{C}$. A generic state $|\chi\rangle$ can be written as a tensor product of the form $\text{(1.15)}$ only if $b_{nm}$ can be factorize as $c_n d_m$.

### 1.2.2 Definition of entanglement

A state vector which cannot be written in the form of a tensor product is termed *entangled state*. Basically, if $|\phi\rangle \in \mathcal{H}_1$ and $|\psi\rangle \in \mathcal{H}_2$, we have that $|\chi\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$ can be

$$ |\chi\rangle = |\phi \otimes \psi\rangle \rightarrow \text{separable} \quad (1.17) $$

$$ |\chi\rangle \neq |\phi \otimes \psi\rangle \rightarrow \text{entangled} \quad (1.18) $$

Entanglement is a phenomenon that has no classical analog. Two entangled objects can be described as a single bipartite state, and whenever we make a measure on one of the two entangled particle we instantly know the outcome on the second one.

As an example consider a qubit, i.e. a two-state quantum system like the spin 1/2 of an electron or the polarization of a photon. In general, $|0\rangle$ and $|1\rangle$ form a basis for our two-dimensional Hilbert space, we will have that a state $|\psi\rangle$ will be in the form

$$ |\psi\rangle = \alpha |0\rangle + \beta |1\rangle \quad (1.19) $$

with $|\alpha|^2 + |\beta|^2 = 1$. Let us now take the two *qubit* entangled state:

$$ |\psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle_1 \otimes |1\rangle_2 - |1\rangle_1 \otimes |0\rangle_2) \quad (1.20) $$

where $|0_1\rangle$ and $|1_1\rangle$ are the basis vector of $\mathcal{H}_1$ and $|0_2\rangle$ and $|1_2\rangle$ are the basis vector of $\mathcal{H}_2$. Let $\hat{S}_1$ be an observable acting on $\mathcal{H}_1^1$, with eigenvectors $|0\rangle_1$ and $|1\rangle_1$. Measuring $\hat{S}_1$ means collapsing the state $|\psi\rangle$ in one of the two
eigenstates of $\hat{S}_1$. That means that if our state collapse in $|0\rangle_1$, the state of the second qubit will immediately collapse in $|1\rangle_2$ and vice versa.

On the other hand consider the state

$$|\phi\rangle = \frac{1}{2}(|0\rangle_1 \otimes |1\rangle_2 + |0\rangle_1 \otimes |0\rangle_2 + |1\rangle_1 \otimes |0\rangle_2 + |1\rangle_1 \otimes |1\rangle_2) \quad (1.21)$$

In this case if we make the same measurement of $\hat{S}_1$ as we did in (1.20), we are not able to define whether the second qubit collapsed on $|0\rangle_2$ or $|1\rangle_2$. If $|\phi\rangle$ collapse in the eigenvector $|0\rangle_1$ after measuring $\hat{S}_1$, we would obtain a new state $|\chi\rangle$ of the form $|\chi\rangle = \frac{1}{2}(|0\rangle_1 \otimes |1\rangle_2 + |0\rangle_1 \otimes |0\rangle_2)$ and we would not know the state of the second qubit.

A state such as (1.21) is called separable and thus the measurement outcomes are uncorrelated.

### 1.2.3 The state operator (or density matrix)

Let us now consider a vector state such that $|\psi\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$. If $|\psi\rangle$ is a tensor product $|\phi_1 \otimes \phi_2\rangle$, then the state vector of particle 1 is $|\phi_1\rangle$. In general, however, a state vector cannot be associated with particle 1: when a quantum system can be described by a vector in a Hilbert space, we are dealing with a pure state. On the other hand, when the information on the system is incomplete, we are dealing with mixed states, i.e. statistical mixture of more states.

Both pure and mixed states can be described mathematically by a density matrix, that is the most general way to represent a state in quantum mechanics\[4\]. We will use this way of representing states later, since we will apply the Schmidt decomposition to density matrices in order to compute the amount of entanglement.

By definition, the density matrix is defined as

$$\hat{\rho} = \sum_n p_n |\phi_n\rangle \langle \phi_n| \quad (1.22)$$

where $|\phi_n\rangle$ are the states involved in the mixture, and $p_n$ are their respective occurrence probabilities, such that $0 \leq p_n \leq 1$ and $\sum p_n = 1$. It is clear to see that if only one state $|\phi\rangle$ is involved (pure state) the density matrix becomes

$$\hat{\rho} = |\phi\rangle \langle \phi| \quad (1.23)$$

Since $\hat{\rho}$ is defined as a state operator, we can now define its matrix form, with elements:

$$\rho_{mn} = \langle m|\hat{\rho}|n\rangle \quad (1.24)$$

The most important properties of $\rho$ are [4]:
1. $\rho$ is Hermitian: $\rho = \rho^\dagger$

2. $\rho$ has unit trace: $\text{Tr}\rho = 1$

3. $\rho$ is semidefinite positive: $\langle \phi | \rho | \phi \rangle \geq 0$

Since the matrix is hermitian, its eigenvalues are real. Furthermore, considering both properties 2 and 3, we find that all eigenvalues must be numbers between 0 and 1, and they add up to 1, just like probabilities.

### 1.2.4 Measurement outcomes

We now want to define a way to calculate the probabilities of measurement outcomes. Given a state $\hat{\rho}$, we define the probability to measure the eigenvalue $a_k$ of the operator $\hat{A}$ as:

$$p(a_k) = \text{Tr}(\hat{\rho} | a_k \rangle \langle a_k|) \quad (1.25)$$

Note that for pure states, such as $\hat{\rho} = |\phi\rangle \langle \phi|$, we obtain the same results of (1.11)

$$\text{Tr}(\hat{\rho} | a_k \rangle \langle a_k|) = \sum_m \langle m | \phi \rangle \langle \phi | a_k \rangle \langle a_k | m \rangle =$$

$$\langle a_k | \sum_m |m\rangle \langle m | \phi \rangle \langle \phi | a_k \rangle =$$

$$\langle a_k | \phi \rangle \langle \phi | a_k \rangle = |\langle \phi | a_k \rangle|^2 \quad (1.26)$$

where $|m\rangle$ is a complete orthonormal basis such that $\sum_m |m\rangle \langle m| = \hat{1}$.

For mixed states the probability of observing $a_k$ will be equal to the product of the probability of being in that state times the probability of measuring $a_k$ in that state. Given $\rho = \sum_n p_n |n\rangle \langle n|$, we have

$$\text{Tr}(\hat{\rho} | a_k \rangle \langle a_k|) = \sum_{m,n} p_n \langle m | \phi_n \rangle \langle \phi_n | a_k \rangle \langle a_k | m \rangle =$$

$$\sum_n p_n |\langle a_k | \phi_n \rangle|^2 \quad (1.27)$$

Now it is clear that the average value of an observable $\hat{A}$, for a mixed state
will be

\[
< \hat{A} > = Tr(\hat{\rho} \hat{A}) = \sum_k \langle a_k | \hat{\rho} | a_k \rangle
= \sum_{n,k} p_n \langle a_k | \phi_n \rangle \langle \phi_n | \hat{A} | a_k \rangle
= \sum_n p_n \langle \phi_n | \hat{A} | \phi_n \rangle
\]

(1.28)

1.2.5 The reduced state operator

Let us now consider a state operator \( \hat{\rho} \) acting in the space \( H_1 \otimes H_2 \) and a physical property we indicate as D depending solely on the first particle. Then the operator associated to D will be of the form \( A \otimes I_2 \), where \( \hat{A} \) acts in \( H_1 \). The expectation value of \( A \otimes I_2 \) will then be

\[
< A \otimes I_2 > = Tr([A \otimes I_2] \rho)
= \sum_{n_1m_1;n_2m_2} \langle n_1 \otimes n_2 | \rho | A \otimes I \rangle | m_1 \otimes m_2 \rangle
= \sum_{n_1m_1;n_2m_2} A_{n_1m_1} \delta_{n_2m_2} \rho_{m_1m_2;n_2n_1}
= \sum_{m_1n_1} A_{m_1n_1} \sum_{n_2} \rho_{m_1n_2;n_2n_1} = \sum_{n_1m_1} A_{m_1n_1} \rho^{(1)}_{m_1n_1} = Tr(A \rho^{(1)})
\]

(1.32)

where \( \rho^{(1)} \) is called reduced the state operator and acts in the first Hilbert space only. In particular the state operator of particle 1 is then given in the form

\[
\rho^{(1)}_{m_1n_1} = \sum_{n_2} \rho_{n_1n_2;n_2m_1} \quad \text{or} \quad \rho^{(1)} = Tr_2 \rho
\]

(1.33)

where \( Tr_2 \) represents the trace on the space \( H_2 \) and acts only on the subsystem of the second Hilbert space \( H_2 \).

1.3 Measures of Entanglement

We now want to give a definition of an entanglement measure. In particular, we want to understand the degree of entanglement for states. A possible way to do it is knowing how much information we would lose on the second particle if we made a measurement on the first one. In this work we will
always be dealing with pure states and one possible measure of entanglement for bipartite pure states is given by the Von-Neumann entropy \[6\].

In particular we associate to each bipartite state a value of quantum entropy, that will be 0 if the state is not entangled and will grow monotonically with the entanglement of states. In our case, the best way to compute the Von-Neumann entropy is using the singular values of the matrix \(b_{nm}\) of Eq.(1.16).

### 1.3.1 Schmidt decomposition

As described in section 1.2.1, each pure bipartite state \(|\chi\rangle\) can be expressed in the form of Eq.(1.16), which we recall being

\[
|\chi\rangle = \sum_{n,m} b_{nm} |n \otimes m\rangle
\]

with \(|n\rangle \in \mathcal{H}_1\) and \(|m\rangle \in \mathcal{H}_2\). The Schmidt decomposition \[4\] is the decomposition of \(|\chi\rangle\) in the singular basis of the matrix \(b\), as we will show below \[4\]. For computing the entanglement, it suffices that we know the singular values \(E_i\) of \(b\). The Schmidt coefficients are defined as \(\lambda_i = E_i^2\). In the singular basis, where to each eigenvector \(|\xi_i\rangle_1 \otimes |\xi_i\rangle_2\) corresponds its singular value \(\sqrt{\lambda_i}\), the state can then be written as

\[
|\chi\rangle = \sum_i \sqrt{\lambda_i} |\xi_i\rangle_1 \otimes |\xi_i\rangle_2
\]

Since the state must be normalized we have \(\sum_i \sqrt{\lambda_i} = 1\).

### 1.3.2 Von-Neumann entropy

We can now introduce the Von-Neumann entropy of reduced state operator as a measure of entanglement. In particular, given a state \(\rho\) we want to find a function \(S(\rho)\) that satisfies some particular axioms, such as

1. \(S(\rho)\) vanishes for separable states
2. additivity: the entanglement of several copies of a state is equal to \(n\) times the entanglement of a single state \(S(\rho^\otimes n) = nS(\rho)\)
3. given two states \(\rho\) and \(\rho'\), it must be \(S(\rho \otimes \rho') \leq S(\rho) + S(\rho')\)
4. convexity: \(S(\lambda \rho + (1-\lambda) \rho') \leq \lambda S(\rho) + (1-\lambda) S(\rho')\)
The basic idea to build this function is that the degree of mixing of a reduced density matrix is related to the amount of entanglement of the pure state $\chi$. Given a reduced state operator in the form of Eq.(1.33), the most prominent choice for this function is the Von-Neumann entropy

$$S(\rho_1) = -Tr(\rho_1 \log(\rho_1)) \tag{1.36}$$

of the reduced density matrix, often simply called as the entanglement E of the pure state $|\chi\rangle$, with $E(|\chi\rangle) = S(\rho)$. Moreover, if $\rho_1$ and $\rho_2$ are the reduced state operators of $\rho$ and the two initial Hilbert spaces have the same dimension, $\rho_1$ and $\rho_2$ have the same non vanishing eigenvalues and it happens that

$$-Tr(\rho_1 \log(\rho_1)) = -Tr(\rho_2 \log(\rho_2)) \tag{1.37}$$

Given a diagonalizable operator $A$ with dimension $k$ it is possible to write its logarithm as

$$\log(A) = V \log(D)V^{-1} \tag{1.38}$$

where $D$ is the diagonal matrix of the eigenvalues of and the columns of $V$ are the normalized eigenvectors of $A$. When an operator $D$ is in its diagonal form, $\log(D)$ is intended to be applied separately to each diagonal element of $D$, such that

$$\log(D) = \sum_i^k \log(d_i) |i\rangle \langle i| \tag{1.39}$$

where $d_i$ are the eigenvalues of $D$. In our case we can write a state operator in its diagonal form through the Schimdt decomposition, such that (recalling Eq.(1.35)) it is

$$|\chi\rangle = \sum_i \sqrt{\lambda_i} |\xi_i\rangle_1 \otimes |\xi_i\rangle_2 \tag{1.40}$$

Thus it is

$$\rho_1 = Tr_2(|\chi\rangle \langle \chi|) = \sum_{n=1}^{d_1} \lambda_n |n\rangle_1 \langle n|_1 \tag{1.41}$$

where $d_1$ is the dimension of the Hilbert space $\mathcal{H}_1$. We can now compute entanglement using Eq.(1.35) as

$$E(|\chi\rangle) = S(\rho) = -Tr(\rho_1 \log(\rho_1)) \tag{1.42}$$

$$= -Tr(\sum_n \lambda_n |n\rangle_1 \langle n|_1 \log(\lambda_n |n\rangle_1 \langle n|_1)) \tag{1.43}$$

$$= - \sum_n \lambda_n \log(\lambda_n) \tag{1.44}$$
In particular, if all Schmidt coefficients, except for 1, are zeros, then the state is separable, otherwise it is entangled [6]. In fact, if a state |φ⟩ in the form of Eq. (1.35) is |φ⟩ = |ξ⟩₁ ⊗ |ξ⟩₂, its entanglement is $E(|ξ⟩) = 1log(1) = 0$, which is consistent with the previous axioms. A state is \textit{maximally entangled} if all the coefficients are of the type $λ_i = 1/d$, where $d$ is the dimension of the smaller of the two subsystem.

Let us now make an example in order to summarize what we have said so far. Consider two Hilbert spaces $\mathcal{H}^A$ and $\mathcal{H}^B$ with eigenvectors $|0⟩_A, |1⟩_A$ and $|0⟩_B, |1⟩_B$ respectively and consider the bipartite state

$$|ψ⟩ = \frac{1}{2}|0⟩_A |1⟩_B - \sqrt{\frac{3}{8}} |0⟩_A |1⟩_B - \sqrt{\frac{3}{8}} |1⟩_A |0⟩_B$$

(1.45)

which implies that the matrix $b_{nm}$ in the form of Eq. (1.34) is

$$
\begin{pmatrix}
\frac{1}{2} & \frac{\sqrt{3}}{8} \\
\frac{\sqrt{3}}{8} & 0
\end{pmatrix}
$$

The singular values of $b$ are then $E_± = ±\frac{1}{2} + \frac{\sqrt{7}}{8}$, with Schmidt coefficients $λ_+ = \sqrt{E_+} ≈ 0.83$ and $λ_- = \sqrt{E_-} ≈ 0.17$. Thus the state is entangled and it happens that $S(|ψ⟩) ≈ 0.51$. 

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2. Tetragonal CuO

We now summarize the chemical and physical properties of CuO, which is a compound from the two elements copper (C) and oxygen (O). Cuprates, i.e. materials that contain Cu-O planes, are interesting materials since they become superconductors at high temperature when 2 electrons are removed from the copper oxide layer, that in our case is composed by a central copper atom with 4 oxygen atoms around it. The correlated electron physics in the CuO layers is probably responsible for the unusual properties of these materials [2]. In particular we can observe the CuO layer described above in Figure 2.1 (example of cuprate) and in Figure 2.2 (focus on the CuO plane).

The goal of this work is studying the quantum correlations that subsist between the holes, the energy of the states that describe the system and their possible dislocation in orbitals.

2.1 History of high temperature superconductors and cuprates

The phenomenon of superconductivity was first discovered in 1911 by Heike Kamerlingh Onnes, who was studying the resistivity of mercury at low temperatures [1]. He discovered that the resistivity dropped to essentially zero for temperatures below 4.2K. Further discoveries followed as physicists tried to discover both other materials that went superconducting at higher and higher temperatures.

At the moment cuprates are the materials that become superconductive at the highest temperature. Studying these materials from a quantum point of view can help us explaining the superconductive nature of these materials.

2.2 CuO structure

Due to the chemistry of the CuO$_4$ layer we are dealing with we can simplify the essential physics of the plane down to that of a three band model, where the copper oxide layer is compromised of 3$d_{x^2-y^2}$, 2$p_x$ and 2$p_y$ orbitals [5]. In its ground state, the copper oxide layer has every copper site occupied by a single hole, so that instead of having 10 electrons on the 3d orbital it only has 9 (3d9) , and every oxygen oxygen site empty of holes, 2p6 [7].

In particular, during this work, we will always analyze a single CuO$_4$
Figure 2.1: Examples of cuprate superconductors. The CuO planes are visible both in $\text{HgBa}_2\text{CuO}_4 + \delta$ and in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$.

plaquette composed by a copper atom in the centre and 4 oxygen atoms around it, as shown in Figure 2.2.

2.2.1 Photoemission process

In its ground state the CuO is missing an electron, which transaltes into a hole. Thanks to a photoemission process we remove another electron and we create a second hole [3].

We show in Figure 2.3 the photoemission spectrum of the second electron from which it is possible to derive the states that describe this system.

2.2.2 Orbitals

Analysis from the photoemission spectra described in 2.2 shows that the quantum bipartite states obtained because of the emission of the second electron can only occupy 3 different type of orbitals[3], which are

1. $3d^8$ orbital - the two holes are both on the copper atom, that loses 2 electrons
2. $3d^9L$ orbital - one hole on the copper atom and one on an oxygen atom
3. $3d^{10}L^2$ orbital - two holes dislocated on the four oxygen atoms
Figure 2.2: CuO plane. Red balls indicate copper atoms, blue balls oxygen. The red squares outlines one CuO plaquette. This picture was taken from the research shown in [2].

Figure 2.3: Photoemission spectrum of the CuO layer in copper oxide. Each line describes a different spectra for different $E_{\text{gap}}$. In our work we will only use the 3 $E_{\text{gap}} = 1.2eV;1.8eV;2.4eV$, defined as the energy to remove an electron for the first ionization state. The spectrum is obtained by measuring the intensity (number of electrons) ejected for relative binding energy. To each energy, a two holes state (represented by a vertical line in the graph) can be associated. We have 59 vertical lines, describing 59 two holes states.
3. Quantum correlations in copper oxide

Let us now introduce the matrix of states obtained from the study of Figure 2.3 in Chapter 2, from which we derive the two hole states (bipartite states) that describe our system. We then compute the entanglement of all states through the Von-Neumann entropy of the reduced state and their projections on the orbitals described in Subsection 2.2.2.

3.1 States and energy gaps

We consider bipartite hole states of CuO. Each hole can occupy one of 8 different energy eigenstates, as described in Figure 3.1. Because we are dealing with spin $\frac{1}{2}$ particles the number of eigenstates is doubled. Since, after the photoemission process we have two holes, the dimension of the Hilbert space of two holes is then $16 \times 16 = 256$.

Because of the Pauli principle, however, we must remove the bipartite states described by two same state with same spin. Moreover we must consider the fact that it is impossible to distinguish between two antisymmetric states. In quantum mechanics, in fact, when we are dealing with fermions we must antisymmetrize the states and thus the allowed states are of the form $|\phi\rangle = \frac{1}{\sqrt{2}}(|m \otimes n\rangle - |n \otimes m\rangle)$, where $n$ and $m$ are the states of the initial Hilbert spaces, each of dimension 16. Finally we have to remove, due to symmetric properties of the system, many other states and in the end we just have 59 possible states describing the two holes of the CuO layer.

It is possible, in physical chemistry, to characterize the state of the molecule (in this case CuO) with a matrix describing the occupancy of all states at once. This matrix is reported in Section 3.10 and its elements depend on the parameters in Figure 3.2.

In particular the most important parameters are:

1. the on-site copper-to-oxygen charge-transfer energy $\Delta_{pd}$
2. the copper-oxygen charge transfer integral for the $b_1$-symmetry $T_{pd}(b_1)$
3. the oxygen-oxygen charge transfer integral $T_{pp}$

These 3 parameters are the ones that we change in our calculations and are responsible for the different values of entanglement that we compute. Notice
Figure 3.1: Energy-level scheme of the basis functions before and after Cu 3d-O 2p-ligand hybridization. It is possible to see the 8 different energy-levels on the right side of the figure. The energy-levels are drawn for parameters values listed in Figure 3.2 for $E_{\text{gap}} = 1.8\text{eV}$. This graph was taken from [3].

<table>
<thead>
<tr>
<th>$E_{\text{gap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{gap}} = 1.2\text{ eV}$</td>
</tr>
<tr>
<td>$\Delta_{pd}$</td>
</tr>
<tr>
<td>$T_{pd}$</td>
</tr>
<tr>
<td>$T_{sp}$</td>
</tr>
<tr>
<td>$A$</td>
</tr>
<tr>
<td>$B$</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>$\eta$</td>
</tr>
<tr>
<td>$\delta$</td>
</tr>
<tr>
<td>$\langle n_d \rangle$</td>
</tr>
</tbody>
</table>

Figure 3.2: Parameter values used to build the matrix of states described in Section 3.1. The first 3 parameters are related to the charge transfer value between atoms. The Racah parameters A,B and C describe the repulsion between the various electrons in the layer of CuO; the last 3 parameters will not be considered in this work since they do not appear in the matrix of states reported in 3.10. This table was taken from article [3].
that in Figure 3.2 also the Racah parameter $A$ changes with different $E_{\text{gap}}$, but, for simplicity, we assume it to be constant in our calculations.

As we shall discuss, we want to see how entanglement changes when we deal with different $E_{\text{gap}}$, defined as the energy needed to remove an electron from the first ionization state plus the energy required to return the electron to the first affinity state.

### 3.2 Symmetry classes

As explained in 3.1, we can use a 59x59 matrix to describe all possible states of the CuO$_2^-$ layer. In particular this matrix is a block matrix, with 7 different blocks. Each block describes a different symmetry class. Here’s the matrix of states with the respective symmetry classes (we named the symmetry classes in the same way as described in the article [3]):

$$
C = \begin{bmatrix}
3A_2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 3E & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1E & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1A_1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1A_2 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 3B_1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1B_1
\end{bmatrix} \quad (3.1)
$$

You can find the matrices describing the symmetry classes we used to compute entanglement in the [3.10](#). The process used to build each of this matrices can be found in [3].

### 3.3 Extraction of single bipartite states

In order to compute entanglement, we first have to separate each state from the matrix (3.1). Our goal is to write states in the form of Eq.(1.34), so that we can apply the Schmidt decomposition and compute their entanglement with Eq.(1.44). Given the tensor product $\mathcal{H}_1 \otimes \mathcal{H}_2 = \mathcal{H}$, with $|m\rangle, |n\rangle \in \mathcal{H}_1$ and $|p\rangle, |q\rangle \in \mathcal{H}_2$ with $\text{dim}\mathcal{H}_1 = \text{dim}\mathcal{H}_2 = 16$ and $|i\rangle, |j\rangle \in \mathcal{H}$, the matrix $C$ describing all possible two hole states can be written as:

$$
C = \sum_{i,j=1}^{256} c_{ij} |i\rangle \langle j| = \sum_{n,m=1}^{16} \sum_{p,q=1}^{16} c_{mn,pq} |m \otimes n\rangle \langle p \otimes q|
\quad (3.2)
$$
where $|i\rangle$ are an orthonormal basis for the 256 two hole states and satisfy the rule $\langle i|j \rangle = \delta_{ij}$. In particular each two particle state $|i\rangle$ can be written as $|i\rangle = |n \otimes m\rangle$ and corresponds to one of the tensor products between the 16 single particle states. In this case $|n\rangle, |m\rangle$ represent the single particles states and should change from 1 to 16 (with $|n\rangle, |m\rangle \in \{|1\rangle, |2\rangle, \ldots , |16\rangle\}$). Note that in principle the matrix C (3.1) is a 256x256 matrix, but since there are a lot of forbidden states as explained above in Section 3.1 we can restrict the matrix to a smaller one containing only non-zero rows and columns. The final C matrix (3.1) can be expressed as a 59x59 block matrix. In order to extract the individual 2-hole states from the matrix C we first have to diagonalize it in the form

$$C = \sum_{k} d_{k} |k\rangle \langle k|$$

(3.3)

where $|k\rangle$ are the eigenvectors of C and $|k\rangle \in \mathcal{H}$. Each eigenvector of C now corresponds to a 2-hole state which is a superposition of states

$$|k\rangle = \sum_{n,m=1}^{16} b_{nm}^{k} |n \otimes m\rangle$$

(3.4)

Finally we have to rewrite each eigenstate in the form of (1.34). In order to do that, we have to identify the states $|i\rangle$ with the states $|m \otimes n\rangle$. So, for example, let us suppose that $|1\rangle = |11\rangle$ and $|2\rangle = |12\rangle$. To complete the matrix b we have to anti-symmetries it. This is due to the fact that we deal with fermionic states that must be anti-symmetric, which means that $b_{nm} = -b_{mn}$.

In order to keep the normalization, we have to divide each off-diagonal element of the matrix b by a factor $\sqrt{2}$, otherwise we would be counting each state two times instead of one.

### 3.4 Energy of states

To begin with, we compute the energy of each state. In the following analysis we will always order states according to their energies (in increasing order within each symmetry class). The energy of each eigenstate $|k\rangle$ (with $|k\rangle \in \{1, 2, 3, ..., 59\}$) in the form of Eq.(3.4) is defined as its eigenvalue $k$, such that $\hat{H} |k\rangle = k |k\rangle$. As we can see from Figure 3.3 each state has 3 different values of energy: this is due to the fact that in our work we use three different $E_{gap}$ to describe our states. Thus changing the eigenstates of the system leads to an alteration of their eigenvalues (i.e. energy of states).
Figure 3.3: Energy of states for the 3 values of $E_{\text{gap}}$ reported in Figure 3.2. Each color defines a symmetry class and circles, triangles, and squares refer to $E_{\text{gap}} = 1.2 \text{ eV}$, $1.8 \text{ eV}$, $2.4 \text{ eV}$ respectively. For each state, increasing $E_{\text{gap}}$ increases its energy. The state with the lowest energy (32) is the so-called Zhang-Rice singlet, which is believed to be the responsible for the superconductive properties of cuprates.
3.5 Entanglement in CuO

Let us now investigate how much the CuO bipartite states obtained through the photoemission process described in Section 2.2.1 are entangled and how their entanglement changes with $E_{\text{gap}}$.

In order to compute entanglement, we first have to rewrite each state in the form of Eq. (3.4) in its singular basis through the Schmidt decomposition, as described in Eq. (1.35). Once we have done that we can calculate the entropy of the reduced state operator using equation Eq. (1.44).

Since the main goal of this work is understanding how entanglement changes within different $E_{\text{gap}}$, Figure 3.4 is the most important graph since it describes the amount of entanglement of each of the two hole states. First of all, we can see in Figure 3.4 how entanglement varies of $\approx 0.5$ unit in function of the $E_{\text{gap}}$ in certain states in the symmetry classes 3A2, 1A2 and 3B1, while it tends not to change ($\approx 0.02$) for the rest of states in classes 3E, 1E, 1A2 and 3B1 (except for states 28 and 29). Moreover, two states have almost vanishing entanglement for $E_{\text{gap}} = 1.2eV$ and $E_{\text{gap}} = 1.8eV$ (states 37 and 55); we will discuss these states later.

In order to better understand the role of entanglement we now want to investigate the orbital projections and charge of all states, focusing in particular on those states with high variations in entanglement in function of $E_{\text{gap}}$. We will then compute the charge on the copper atom for each of these states and we will compare entanglement with the charge of states.

3.6 Projections on orbitals

As discussed in Section 2.2.2 states in the $CuO_2^-$ layer are dislocated in 3 different orbitals. Thus each state can be written as a linear superposition of these orbitals. Basically, given a state $|\psi\rangle$ of the form of Eq. (3.4), we can write it in the orbital basis as

$$|\psi\rangle = a |3d8\rangle + b |3d9L\rangle + c |3d10L2\rangle$$

(3.5)

with $a, b, c \in \mathbb{C}$ such that $|a|^2 + |b|^2 + |c|^2 = 1$. Let’s, for example, consider the 3d8 orbital. The probability $p_{3d8}(\psi)$ to find the state $|\psi\rangle$ in this orbital is

$$p_{3d8}(\psi) = |\langle 3d8|\psi\rangle|^2 = |a|^2$$

(3.6)

Since the projections have to be normalized, it will also be true that

$$p_{3d8}(\psi) + p_{3d9L}(\psi) + p_{3d10L}(\psi) = 1$$

(3.7)
Figure 3.4: Entanglement of states for the 3 values of $E_{gap}$ reported in Figure 3.2. Each color define a symmetry class and circles, triangles and squares refer to $E_{gap} = 1.2eV, 1.8eV, 2.4eV$ respectively. Inside each symmetry class the states are ordered in terms of increasing energy (cf. Figure 3.2).
for all states.

The first orbital we want to analyze is the 3d8, which, as explained in 2.2.2, contains 2 holes on the copper atom. As we can see from Figure 3.5, inside each symmetry class, except for 1A2 (orange) and 3B1 (black) classes, the states with the highest components of 3d8 are the "last states", i.e. those states with the highest energies. We also observe that states with lower energies do not vary significantly their projections, which means that they are characterized by small differences in their projection values in function of the $E_{gap}$. These low energy states vary their projection of a factor $\pm 0.1$, while the middle and high energy states undergo a medium variation of $\pm 0.3$ unit.

Interestingly we can see from Figure 3.5 that states in the 1A2 (orange) and 3B1 (black) classes behave in the opposite way compared to other classes. Low energy states have in fact a large projection on 3d8, while the high energy states have a projection smaller than $\approx 0.2$.

Before studying the correlation between entanglement and projections we
Figure 3.6: 3d9L Projections. States are divided by colors in symmetry classes: 3A2 (red), 3E (brown), 1E (blue), 1A1 (purple), 1A2 (orange), 3B1 (black), 1B1 (magenta). Each state has 3 different values of projection on 3d9L, referring respectively to $E_{\text{gap}} = 1.2eV$ (circles), $E_{\text{gap}} = 1.8eV$ (triangles) and $E_{\text{gap}} = 2.4eV$ (squares).
Figure 3.7: 3d10L2 Projections. States are divided by colors in symmetry classes: 3A2 (red), 3E (brown), 1E (blue), 1A1 (purple), 1A2 (orange), 3B1 (black), 1B1 (magenta). Each state has 3 different values of projection on 3d10L2, referring respectively to $E_{gap} = 1.2eV$ (circles), $E_{gap} = 1.8eV$ (triangles) and $E_{gap} = 2.4eV$ (squares).
want to analyze the projections of state on 3d9L and 3d10L2 orbitals. Let’s focus on the 3d9L orbital first, that is described by one hole on the copper atom and one hole on one of the oxygen atoms. As we can see from Figure 3.6 the behavior of states is the opposite of the one discussed for the 3d8 projections. In this case in fact low energy states have a huge component (more than 0.6) on this particular orbital, while high energy states have a small projection on 3d9 (less than 0.4). Again the states in the 1A2 and 3B1 classes behave in the opposite way.

In this particular case the projection of states on 3d9L is hardly depending on $E_{\text{gap}}$, with only a few states (25 and 39) with a difference on their projection higher than $\approx 0.2$ unit. If there was a correlation between entanglement and projection on 3d9L, we would expect a strong variation in terms of projection in function of the $E_{\text{gap}}$ for those states whose entanglement changes in function of $E_{\text{gap}}$ (3A2,1A1 and 1B1 classes). Obviously if none of the 3d9L or 3d8 orbital are related to entanglement in function of the $E_{\text{gap}}$, it turns out that neither the projections on 3d10L2 are correlated, since each projection is strongly dependent on the other two by Eq.(3.7).

Moving to the 3d10L2 projections, shown in Figure 3.7, it is possible to see how in this case the states with the highest components in this orbital are the middle states, i.e. those states with an average energy. Contrary to what happened before in this case also the 1A2 and 3B1 classes behave likewise the others.

We now want to study in details the correlation between entanglement and projection of states on orbitals in function of $E_{\text{gap}}$. Since in Figure 3.4 we discussed how certain classes (like 3E, 3B1 and 1A2) contain states whose entanglement does not change, if there was a correlation we would expect a similar behavior for their projections in function of $E_{\text{gap}}$. In order to evaluate this we decide to focus on the projections of two classes (3E and 1A1) whose behavior in terms of entanglement is definitely different. In particular in the 3E class we observe a small variation of entanglement in terms of $E_{\text{gap}}$, while in the 1A1 class entanglement varies significantly (view Figure 3.9).

Observing Figure 3.8 we can notice that states inside these symmetry classes have an overall common behavior. In fact the first states (1-6) have a low component in the 3d8 orbital while the last states (7-12) have a large component in the 3d8 orbital, with evident variations in function of the $E_{\text{gap}}$ compared to the first.

Thus the two classes show a similar behavior in terms of projections on 3d8, while they show a completely different behavior in terms of entanglement as a function of $E_{\text{gap}}$ (view Figure 3.9).

This comparison between Figures 3.8 and 3.9 leads us to the conclusion that there is not a correlation between entanglement and projections on 3d8.
Figure 3.8: Focus on 3E and 1A1 projections on 3d8. Circles, triangles and squares refer to $E_{\text{gap}} = 1.2\text{eV}; 1.8\text{eV}; 2.4\text{eV}$ respectively. As we can see from the comparison of the two Figures (a) and (b) the overall behavior of states is similar.

Figure 3.9: Focus on 3E and 1A1 entanglement. Notice that, even though the scale on the y axis is different, the behavior of states is still evident, with states on 3E that are almost not affected by $E_{\text{gap}}$ compared to states in 1A1.
Table 3.1: Summary of the value of the energy, entanglement and the largest value of the projection on the 3d9L, 3d10L2, and 3d8. The correspondence is within each symmetry class (c.f. Eq. (3.1) and Figs. 3.3, 3.4, 3.5-3.7).

in terms of $E_{\text{gap}}$. In fact, despite Figures (a) and (b) in Figure 3.8 show a similar behavior, the same states in terms of entanglement show a completely different behavior ((a) and (b) in Figure 3.9).

Even though no correlation with entanglement is highlighted, Figures (a) and (b) in Figure 3.8 show a strong dependence of projection on 3d8 with energy. Recall that states are ordered by increasing energy within each symmetry class which means that states with higher energy have a higher projection on 3d8.

In order to summarize what we observed so far we can observe Table 3.2 with the main feature of states inside each symmetry class.

3.7 Charge on copper atom

Beside the projections we can calculate the average charge carried on the copper atom. For 3d8 there are 8 electrons on the copper, for 3d9L there are 9 and in the end for 3d10L2 there are 10. Thus, given a state in the basis $|\psi\rangle = a |3d8\rangle + b |3d9L\rangle + c |3d10L2\rangle$, the average charge is

$$Q(|\psi\rangle) = 8|a|^2 + 9|b|^2 + 10|c|^2$$

(3.8)

This means that, since $a, b, c$ go from 0 to 1 and are normalized, i.e. $|a|^2 + |b|^2 + |c|^2 = 1$, the highest possible value for charge is 10, when all the state lies in the 3d10L2 orbital.

We decided to focus in particular on those classes with larger variations of entanglement, which are the 3A2, 1A1 and 1B1 classes, because they show an evident affection by $E_{\text{gap}}$. As we can see from Figure 3.10 the states with the highest charge on copper are the middle states, i.e. the central states of the respective symmetry class when ordered in terms of energy. This is expected since we discussed through Figure 3.9 how middle states are the ones that have their higher component on the 3d10L2 orbital.
Figure 3.10: Charge on the copper atom for 3A2, 1A1 and 1B1 symmetry classes. These classes are the most interesting from the entanglement variation point of view.

Interestingly the state with the highest charge are the one with the lowest entanglement.

Let us report a focus of Figure 3.4 of these symmetry classes. If we compare the charge of state (4) in function of $E_{\text{gap}}$ in the 3A2 class and we compare it with the results in Figure 3.13 we observe that, for $E_{\text{gap}} = 1.2\,\text{eV}$, to the highest charge state corresponds the lowest value of entanglement. This argument applies in the same way to state (6) in the 1A1 class and to state (4) in the 1B1 symmetry. Moreover state (4) in the 3A2 class shows a high difference of charge in function of $E_{\text{gap}}$ compared to other states. This feature translates into a deep variation in entanglement, too. As we can see from Figure 3.11 the 1A1 class contains another interesting state (5). We observe that when we lower the $E_{\text{gap}}$ the entanglement value becomes smaller, too, while instead the charge increases (view Figure 3.10).

Theses states that we are focusing on (circled states in Figures 3.11,3.12,3.13) have high charge, which translates into a high component in the 3d10L2 orbital (view Figure 3.7). Although, in fact, they have a medium energy inside the respective classes (view Figure 3.3), the reason of these low values of entanglement (Figure 3.11, 3.12, 3.13) may be connected with the geometry of the system. The 3d10L2 orbital is characterized by the fact that both of the holes are on the oxygen atoms, as discussed in Section 2.2.2. Thus the
Figure 3.11: Entanglement in 1A1 class. Circled states have a low entanglement value and are the ones who are affected the most by $E_{\text{gap}}$.

Figure 3.12: Entanglement in 1B1 class. State (4) is one of the states with vanishing entanglement for $E_{\text{gap}} = 1.2\text{eV}$. This state undergoes a large variation of entanglement in function of $E_{\text{gap}}$, too.
Figure 3.13: Entanglement in 3A2 class. State (4) is the most interesting in this class since its entanglement varies a lot in function of $E_{\text{gap}}$.

holes could occupy a wider space and be less correlated compared to state with high component in the other orbitals.

We conclude that to states with low entanglement correspond states with high charge, especially when the $E_{\text{gap}}$ is low.

3.8 1E class low entangled state

In Section 3.7 we discussed in details only those classes where entanglement changes significantly in function of $E_{\text{gap}}$. We now want to make a similar discussion for the other classes and in particular we will now analyze the 1E class. If we look at Figure 3.4 we can see that, for the majority of its states, the 1E class is one of the most stable (small variation compared to the other) classes in terms of $E_{\text{gap}}$ variations. Nevertheless there is a state whose entanglement changes a lot compared to the others.

As we can see from Figure 3.9 this state has the highest component in the 3d10L2 orbital, which means that has a high charge, too. We report in Figure 3.14 and Figure 3.15 the charge and entanglement graph for the entire symmetry class. Interestingly, this state (9) has the highest charge compared to all other states for $E_{\text{gap}} = 1.2eV$ (see Figure 3.14) which corresponds to the lowest value of entanglement for all states and for all $E_{\text{gap}}$ inside the symmetry class (Figure 3.15).
Figure 3.14: Charge on copper atom for states in 1E symmetry class. The largest value of charge is observed in states (8) and (9). These states have the largest value of charge for $E_{\text{gap}} = 1.2\text{eV}$.

Figure 3.15: Entanglement focus on 1E class. State (9) shows an evident variations in terms of entanglement compared to the other states in this class. Moreover the lowest amount of entanglement corresponds to the lowest $E_{\text{gap}}$. 
Figure 3.16: Charge of states in the case of $E_{\text{gap}} = 1.2 \text{eV}$. The circled states are the ones we focus on since they have a high charge.

### 3.9 High charged states

In Section 3.7 and 3.8 we discussed how low entangled states correspond high values of charge. In particular, starting from Figure 3.4, we took into consideration states with low entanglement and found that they all have high energy values. We now want to proceed in the opposite direction and verify whether high charged states correspond low entangled values or not. In particular we will focus on the charge of states for $E_{\text{gap}} = 1.2 \text{eV}$ since from our previous considerations only in this case a correlation between charge and entanglement is highlighted.

In Figure 3.16 it is reported the charge of states for all symmetry classes. As we can see from Figure 3.16, in the 1A1 symmetry there are four states (that occupy the central part of the graph 35-38) with a high value of charge in the case of $E_{\text{gap}} = 1.2 \text{eV}$. If we look at Figure 3.11, however, only two of them have a low value of entanglement, while the other two (7 and 8 in Figure 3.11) show an average entanglement in respect of the other states in the class. In the 1B1 class there are two states with high charge values (view Figure 3.16 and 3.10) but only one state in this class has low entanglement (almost vanishing for the $E_{\text{gap}}$ considered) as we can see from Figure 3.12.
A similar argument can be made for states in the 1E class. Again, if we look at Figure 3.14 we observe three states (7, 8, 9) with high charge, but only one of them (9) shows a low amount of entanglement in the case of $E_{\text{gap}} = 1.2\text{eV}$.

Observing Figure 3.16 we notice that there are two states in the 3E class with an above average charge value. Recalling Figure 3.9 (a), however, we already discussed how this class is characterized by high values of entanglement with small variations in terms of $E_{\text{gap}}$. A similar consideration can be made for the second state in the 1A2 class (orange). Again, as we can see from Figure 3.4 this class behaves in a similar way of the 3E class and no low entanglement state is observed.

The only classes that show a two-way correspondence between high charge and low entanglement are the 3A2 and 3B1. In the 3A2 class we observe only one state with a high value of charge which translates into a low value of entanglement, as already discussed in Section 3.7. In the 3B1 class, instead, we do not observe either high charged or low entangled states.

To summarize what we have observed in this work let us report a table describing the correlations between charge and entanglement in the case of $E_{\text{gap}} = 1.2\text{eV}$.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>#3A2</th>
<th>#3E</th>
<th>#1E</th>
<th>#1A1</th>
<th>#1A2</th>
<th>#3B1</th>
<th>#1B1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low entanglement</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>High charge</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Biunique correspondence</td>
<td>T</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>T</td>
<td>F</td>
</tr>
</tbody>
</table>

Table 3.2: Summary of the correspondence between low entangled and high charged states. In the first two lines we report the number of states that satisfy the left rule in each symmetry class, in the third line we discuss whether the biunique correspondence is respected (True) or not (False).
Conclusion

The aim of this work was to investigate the role of entanglement in CuO$_2$ layers of CuO.

In Chapter 1 we discussed the basic theoretical concepts of tensor products, introducing the main quantum properties of entangled states and giving a definition of measure of entanglement. Subsequently in Chapter 2 we introduced cuprates and in particular CuO, explaining why we were interested in this particular material. We discussed the photoemission process through which we got the quantum states we analyzed in Chapter 3 and discussed the various orbitals that characterize this molecule.

Finally in Chapter 3 we computed entanglement and studied how it changes in function of the $E_{\text{gap}}$. In order to understand better the behavior of entanglement in states we also studied their projections on the different orbitals, the charge on states and their energy. We observed that, in terms of entanglement in function of $E_{\text{gap}}$ states behave differently in respect of the symmetry class they belong to. We then discussed how, if taken individually, projections were not correlated with entanglement. We found out, however, that the 3d8 projections are strictly correlated to the energy of states, pointing out the fact that the dislocation of holes in the 3d8 case could be the cause of this correlation.

Subsequently we considered all 3 orbital projections at once by computing the charge on the copper atom, defined as Eq. (3.8), and we showed how to low entangled states correspond an high value of charge, especially in the case of low $E_{\text{gap}}$. Finally we studied the opposite implication (high charged states corresponding to low entanglement states) and we find out that this feature is not a biunique correspondence.

We conclude by stating that our results showed that low entangled states are characterized by the highest values of charge, especially when we are dealing with $E_{\text{gap}} = 1.2\,\text{eV}$ even though the opposite implication is not always correct. Moreover a state that is believed could be playing a role in the superconductive properties of CuO is the lowest energy state in the 1A1 symmetry, i.e. the Zhang-Rice singlet. A more detailed study on this state could help us understanding more the physics behind these materials.
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Appendix

### 3.10 Symmetry classes

Here are reported the class matrices with the respective parameters used to compute entanglement:

3A2=

\[
\begin{array}{cccccccc}
AA+4B & Tb1 & Tb2 & 0 & 6B & 0 & 0 \\
Tb1 & -A+Db1 & 0 & Tb2 & 0 & 0 & 0 \\
Tb2 & 0 & -A+Db2 & Tb1 & 0 & 0 & 0 \\
0 & Tb2 & Tb1 & -2A+Db1+Db2+Upp & 0 & 0 & 0 \\
6B & 0 & 0 & 0 & AA-5B & 1.141Te & 0 \\
0 & 0 & 0 & 0 & 1.141Te & -A+De & 1.141Te \\
0 & 0 & 0 & 0 & 0 & 1.141Te & 2(-A+De)+Upp \\
\end{array}
\]

3E=

\[
\begin{array}{cccccccc}
AA-5B & Te & Tb1 & 0 & dd1 & 0 & 0 & 0 & dd2 & 0 & 0 & 0 \\
Te & -A+De & 0 & Tb1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & Tb1 & P & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
dd1 & 0 & 0 & 0 & AA+B & Te & Ta1 & 0 & dd1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & Te & -A+De & 0 & Ta1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & Ta1 & 0 & -A+Da1 & Te & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & Ta1 & P & 0 & 0 & 0 & 0 \\
dd2 & 0 & 0 & 0 & dd1 & 0 & 0 & 0 & AA-5B & Te & Tb2 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Te & -A+De & 0 & Tb2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Tb2 & 0 & -A+Db2 & Te \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Tb2 & -A+Db2 & Te & -2A+Db2+De+Upp \\
\end{array}
\]

1E=

\[
\begin{array}{cccccccc}
AA+B+2CC & Te & Tb1 & 0 & dj1 & 0 & 0 & 0 & dj2 & 0 & 0 & 0 \\
Te & -A+De & 0 & Tb1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & Tb1 & Q & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
dj1 & 0 & 0 & 0 & AA+3B+2CC & Te & Ta1 & 0 & dj1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & Te & -A+De & 0 & Ta1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & Ta1 & 0 & -A+Da1 & Te & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & Ta1 & Q & 0 & 0 & 0 & 0 \\
dj2 & 0 & 0 & 0 & dj1 & 0 & 0 & 0 & AA+B+2CC & Te & Tb2 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Te & -A+De & 0 & Tb2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Tb2 & 0 & -A+Db2 & Te \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Tb2 & -A+Db2 & Te & Q \\
\end{array}
\]
Parameters are expressed in Figure 3.2. We added the following ones, depending solely on parameters in Figure 3.2

- $P = \text{Te} - 2A + Db1 + \text{De} + \text{Upp}$
- $Q = -2A + Db1 + \text{De} + \text{Upp}$
- $R = 2(-A + Da1) + \text{hole} + \text{Upp}$
- $Da1 = \Delta + Tpp$
- $Db1 = \Delta - Tpp$
- $Db2 = \Delta + Tpp$