Bulk and Surface Nanoscale Hole Density Inhomogeneity in HgBa$_2$CuO$_{4+\delta}$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ Cuprates

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It is well established that the hole density in the prototypical superconductor La$_{2-x}$Sr$_x$CuO$_4$ is very inhomogeneous due to Sr-dopant induced disorder. On the other hand, the hole distribution in HgBa$_2$CuO$_{4+\delta}$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ doped by interstitial oxygen is believed to be much more uniform. Recent nuclear magnetic resonance measurements indicate, however, that the charge inhomogeneity in HgBa$_2$CuO$_{4+\delta}$ is close to that in La$_{2-x}$Sr$_x$CuO$_4$. Calculations performed in the present paper confirm this observation. We also show that the charge inhomogeneity is most pronounced at the surface layer that can be probed by scanning tunneling microscope. Our simulations demonstrate that, despite having similar amplitudes of charge inhomogeneity, the hole mean free path in HgBa$_2$CuO$_{4+\delta}$ is substantially longer than that in La$_{2-x}$Sr$_x$CuO$_4$. The screening of the Coulomb repulsion in HgBa$_2$CuO$_{4+\delta}$ is also stronger. These two reasons might explain the difference in the superconducting critical temperatures between these two compounds.

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I. INTRODUCTION

The nanoscale electronic disorder is a long standing problem in physics of cuprates. This problem has many aspects, among which the most important one is the influence of disorder on critical temperature $T_c$. Since the energy scale associated with pairing mechanism in CuO$_2$ plane is believed to be universal, different out-of-plane defects are expected to influence $T_c$ differently.$^{1,2}$ Another important aspect is the nanoscale inhomogeneity of the local density of states (DOS) measured by scanning tunneling microscope (STM). This effect was mostly studied$^{3,4}$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. In this paper, we address theoretically the problem of the nanoscale charge inhomogeneity in cuprates, and a related issue of the hole mean free path. We focus on two single layer families of high-$T_c$ superconductors, La$_{2-x}$Sr$_x$CuO$_4$ and HgBa$_2$CuO$_{4+\delta}$, in which the density inhomogeneity has been quantified by nuclear quadrupole resonance (NQR) experiments.$^{5,6}$ We also calculate the charge inhomogeneity in the surface layer of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$.

The NQR measures the energy splitting of nuclear levels induced by an electric field gradient at the nucleus. A hole in the 3d-shell of the Cu ion gives a dominant contribution to the field gradient at the Cu nucleus. The Cu NQR frequency in cuprates is therefore very sensitive to the doping level and is directly proportional to the local hole concentration. The contribution of the 3d-hole to the field gradient is significantly compensated by contributions of holes located at nearby oxygens,$^{8,9}$ therefore the slope of the NQR frequency versus doping varies among different cuprate families.

It is widely accepted that the hole density distribution within the CuO$_2$ layer in La$_{2-x}$Sr$_x$CuO$_4$ is very nonuniform, as it has been clearly demonstrated by measurements of $^{65}$Cu NQR spectra.$^{10}$ The observed broad NQR spectrum$^{10}$ unambiguously indicates a very inhomogeneous hole density profile in the bulk of the sample. The inhomogeneity is due to the doping mechanism, where Sr substitutions of La ions create an effective Coulomb defect very close to the conducting CuO$_2$ plane. In a recent paper$^{11}$ we have performed the Hartree-Fock simulation of the charge density distribution in La$_{2-x}$Sr$_x$CuO$_4$, which shows a very inhomogeneous charge density profile at the nanometer scale, and reproduces the observed NQR lineshapes.

On the other hand, it is generally believed that hole density distribution in compounds doped by interstitial oxygens, such as HgBa$_2$CuO$_{4+\delta}$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, is much more uniform than in La$_{2-x}$Sr$_x$CuO$_4$. This is because the distance from the interstitial oxygen to the CuO$_2$ layer is typically larger than the Sr-layer distance in La$_{2-x}$Sr$_x$CuO$_4$. However, Cu NQR measurements in the single layer HgBa$_2$CuO$_{4+\delta}$ as well as in the bilayer HgBa$_2$CaCu$_2$O$_{6+\delta}$ show fairly large linewidths comparable to that in La$_{2-x}$Sr$_x$CuO$_4$. As it will be demonstrated below, the NQR data imply the same degree of the hole density inhomogeneity in La$_{2-x}$Sr$_x$CuO$_4$ and HgBa$_2$CuO$_{4+\delta}$. We will also show that despite having similar amplitudes of the charge inhomogeneity, the spatial profiles of the density distribution are very different in these two cases: it is much smoother in the oxygen doped HgBa$_2$CuO$_{4+\delta}$. Consequently, the forward scattering is predominant and the mean free path in HgBa$_2$CuO$_{4+\delta}$ is substantially longer than that in La$_{2-x}$Sr$_x$CuO$_4$. Our simulation also indicates that the screening of the Coulomb repulsion between the charge carriers in HgBa$_2$CuO$_{4+\delta}$ is stronger. We argue that these two reasons might explain the difference in superconducting critical temperatures between these two compounds.

The nanoscale charge density inhomogeneity in under-doped cuprates is an indirect way to distinguish the large Fermi surface of a normal Fermi liquid and the small
Fermi surface of a doped Mott insulator. Calculations in Ref. 10 for La$_{2-x}$Sr$_x$CuO$_4$ were based on the small hole pocket Fermi surface, which implies a small number of mobile charge carriers. The small number of charge carriers results in poor screening and hence in the strong charge density inhomogeneity consistent with NQR data. On the other hand, the large Fermi surface implies the large number of mobile charge carriers and a very effective Coulomb screening. In this case calculations give a very moderate charge inhomogeneity, which is too weak to explain the observed NQR linewidths. Hence the screening at the surface is weaker and this results in the stronger charge inhomogeneity.

Another important point is that the charge inhomogeneity in the surface layer is always stronger than that in the bulk layer. This is because the surface ionic dielectric constant is about two times smaller than that in the bulk. Hence this results in the stronger charge inhomogeneity.

In this paper, we present Hartree-Fock calculations in underdoped cuprates with realistic parameters to simulate the bulk charge distributions in HgBa$_2$CuO$_{4+δ}$ and La$_{2-x}$Sr$_x$CuO$_4$, and the surface charge distribution in Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$. Our calculation covers from underdoped to optimally doped regime. We fine tune theoretical parameters to reproduce experimentally known NQR linewidths. This enables us to perform a very accurate comparison of HgBa$_2$CuO$_{4+δ}$ and La$_{2-x}$Sr$_x$CuO$_4$. We find the charge inhomogeneity of a similar scale in both cases. However, the landscapes of spatial modulations and the hole mean free paths are substantially different. This is due to different positions of the dopant oxygen and the Sr-ion relative to the CuO$_2$ plane. In addition, the dielectric constants in these two compounds are different.

Motivated by STM data in Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$, we calculate also the hole density distribution in the surface CuO$_2$ layer of this compound. The results obtained show a large charge density inhomogeneity comparable to that in the bulk of HgBa$_2$CuO$_{4+δ}$. Naturally, the local charge density is highly correlated with the interstitial oxygen positions as has been noticed previously.

Structure of the paper is the following: in Sec. II we formulate the effective model for an isolated CuO$_2$ layer. Because of the long-range nature of the Coulomb interaction, however, the isolated layer approximation is not sufficient and one has to take into account other layers. The impact of the other layers depends on the way of doping and on structural details: whether this is a single layer or a double layer compound. The single layer La$_{2-x}$Sr$_x$CuO$_4$ and HgBa$_2$CuO$_{4+δ}$ are considered in Section III. In Sec. IV we simulate the charge distribution on the surface of the double layer Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$. We also calculate the correlation function between the local charge density and oxygen dopant positions, and compare the result with the local DOS correlation function measured by STM. Our conclusions are presented in Sec. V.

II. THE EFFECTIVE MODEL FOR A CuO$_2$ PLANE

We adopt the effective model formulated in Ref. 11 based on the picture of a lightly doped Mott insulator. Throughout the paper we denote the average hole concentration by $p$ and assume $p ≪ 1$. The central point is that the number of charge carriers is $p$ instead of $1 − p$ as one would expect for a normal Fermi liquid. We consider first an “isolated” CuO$_2$ layer. The “isolated” means that we disregard screening effects of the other layers.

To construct a model relevant to cuprates, we first notice that there are the following distinct length scales: (i) The scale of the order of 1-2 lattice spacing where the doped holes are dressed by multiple virtual magnons. (ii) The scale about average separation between Coulomb defects or average separation between holes $\sim 1/\sqrt{p}$. This is the scale of the Coulomb screening. (iii) The scale $r \gg 1/\sqrt{p}$. The Coulomb gap may develop at this scale due to Anderson localization effects.

Regarding the first point, we do not treat the strong correlations explicitly, but instead adopt the effective hole dispersion after quantum fluctuations at short distances are included. To stress this point, we frequently use the term “holon” instead of “hole”. It is known that the holon dispersion has minima at momenta $k_0 = (±\pi/2, ±\pi/2)$, and is approximately isotropic around these points. The bandwidth of the holon is about $2J$, where $J \approx 130$ meV is the superexchange in the $t$-$J$ model, although we do not directly employ the $t$-$J$ formalism. Hereafter we set the following energy and distance units

\[ J = 130 \text{ meV} \to 1, \]
\[ a_0 = 0.38 \text{nm} \to 1, \]  

where $a_0$ is the lattice spacing of the CuO$_2$ plane. To imitate the holon dispersion we consider spinless fermions on a 2D square lattice. The Hamiltonian reads as follows:

\[ H_t = \sum_{\langle ij \rangle} t'' c^\dagger_i c_j, \]  

where $c^\dagger_i$ is the holon creation operator at site $i$, and $t''$ denotes the next-next-nearest-neighbor hopping on the square lattice. The Hamiltonian yields the following dispersion

\[ \epsilon_k = 2t''(\cos 2k_x + \cos 2k_y). \]  

The dispersion is isotropic around minima at $k_0 = (±\pi/2, ±\pi/2)$ as shown in Fig. 1. We choose $t'' = 0.25J$ to reproduce the realistic holon bandwidth, about $2J$, as obtained from numerical simulations of the $t$-$J$ model. An additional argument supporting this value is as follows. Near its minimum the dispersion can be expanded as $\epsilon_k = const + 4t''|k - k_0|^2$, so the holon effective mass is equal to $m^* = h^2/(8\pi^2 t'')$. The value $t'' = 0.25J$ results in the effective mass $m^* \approx 2m_e$
which is close to the effective mass measured in magnetic quantum oscillation experiments. The realistic holon band width and the realistic effective mass justify our choice of $t'' = 0.25J$. We note also that in the original $t$-$J$ model formalism, there are four holon half-pockets inside magnetic Brillouin zone, and each pocket has two pseudospins; in the present model, we consider four full pockets inside the full Brillouin zone with spinless fermions, hence the number of charge degrees of freedom is exactly the same.

Even though the holes are heavily dressed by magnetic fluctuations, their charge is conserved and hence they interact with Coulomb defects via the ordinary Coulomb potential:

$$H_{h-O} = \sum_{i,j} U_{ij} c_i^\dagger c_i^\dagger c_j c_j,$$

$$U_{ij} = -Q \frac{1}{\sqrt{|\mathbf{R}_{ij} - \mathbf{r}_i|^2 + a^2_{ih}}},$$

$$a^2_{ih} = a^2_{ZR} + \lambda^2. \quad (4)$$

Here $\mathbf{r}_i$ is position of the holon and $\mathbf{R}_{ij}$ is the in-plane projection of the Coulomb defect (Sr-ion or dopant oxygen) position. The distance from the plane to the defect is $\lambda$, and $a_{ZR} \approx 0.8$ is the size of the Zhang-Rice singlet. (We recall that the energy and distances are given in units of $J$ and $a_0$, correspondingly). The dimensionless “charge” $Q \sim 0.5$ depends on the compound, and we discuss its precise values later.

Holon-holon Coulomb interaction is of a similar form

$$H_{int} = \sum_{ij} U_{ij} c_i^\dagger c_i^\dagger c_j c_j,$$

$$U_{ij} = \frac{Q}{\sqrt{|\mathbf{r}_i - \mathbf{r}_j|^2 + a^2_{hh}}}, \quad (5)$$

where $a^2_{hh} \approx 2a^2_{ZR} \approx 1$ stands for the combined size of two Zhang-Rice singlets.

The total Hamiltonian

$$H = H_t + H_{h-O} + H_{int}, \quad (6)$$

describes the in-plane Coulomb problem. Since the Coulomb interaction is not very strong, we solve the many-body problem with the Hamiltonian using the standard Hartree-Fock method. In other words we use the Hartree-Fock decomposition of the Coulomb interaction between holons:

$$H_{int} \rightarrow \sum_{ij} U_{ij} c_i^\dagger c_i^\dagger c_j c_j - \sum_{ij} U_{ij} (c_i^\dagger c_j)(c_j^\dagger c_i). \quad (7)$$

This can be done for zero as well as for finite temperatures, as it is described in Ref. 10.

The above formulation would solve the Coulomb problem for the “isolated” CuO$_2$ layer. However, the layer is always embedded in a multilayer structure, and because of the long-range nature of the Coulomb interaction, we have to take into account other layers. Their influence depends on the lattice structure. In the next section, we consider two different families of single layer cuprates.

III. SINGLE LAYER HgBa$_2$CuO$_4$ AND La$_{2-x}$Sr$_x$CuO$_4$ COMPOUNDS. CHARGE DENSITY DISTRIBUTION, NQR LINE SHAPE, DENSITY OF STATES

We treat a particular CuO$_2$ plane using the Hartree-Fock (HF) method. The role of other CuO$_2$ planes is to provide screening of the Coulomb interaction in the Hartree-Fock analysis. Since CuO$_2$ planes have a very high longitudinal polarizability we consider the “other planes” as purely metallic. It has been shown in Ref. 11 that this “metallic approximation” is valid at $p > 1 - 2\%$ when the polarizability is sufficiently high. Within this approximation the HF plane in a single layer compound is sandwiched between two “metallic” sheets, as demonstrated in Fig. 2 for La$_{2-x}$Sr$_x$CuO$_4$.
A. \textbf{La}_{2-x}\text{Sr}_x\text{CuO}_4

Coulomb defects in \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 are created by Sr substitution for La ions. Therefore each defect donates one hole

\[ p = x. \quad (8) \]

Given the periodic structure of \text{CuO}_2 planes along $c$–axis, there are two layers of Sr defects between two neighboring \text{CuO}_2 planes, as shown in Fig. 2. We mark the defect layers by the index $m = \{1, 2, 3, 4\}$, so the HF \text{CuO}_2 plane is under the influence of 4 layers of Sr defects. Concentration of defects in each defect layer is $x/2$. The planar positions of defects are assumed to be random, and defects are assumed to sit above the center of the Cu plaquette. In addition, in each defect layer we impose a condition that defects never sit next to each other, i.e., the distance between defects is always larger than $\sqrt{2}$. The distance between \text{CuO}_2 layers is $d = 1.75$, and the geometric distances to Coulomb defects are $\lambda_1 = \lambda_4 = 1.15$, $\lambda_2 = \lambda_3 = 0.6$. After accounting for the screening by “metallic” planes, the holon interaction with a defect \cite{10} is replaced by

\[ U_{i}^{m} \rightarrow -Q \left( \frac{1}{\sqrt{|R_{i} - r_{i}|^2 + a_{dm}^2}} \right) \]

\[ + \sum_{n=1}^{\infty} \frac{(-1)^n}{\sqrt{|R_{i} - r_{i}|^2 + (2nd + \lambda_m)^2}} \]

\[ + \sum_{n=1}^{\infty} \frac{(-1)^n}{\sqrt{|R_{i} - r_{i}|^2 + (2nd - \lambda_m)^2}} \].

The summation over $n$ reflects the image method for metallic screening\cite{10}. With values of the distances $\lambda$ given above, the parameter $a_d$, defined in Eq. \cite{11}, takes the following values: $a_{d1} = a_{d4} = 1.4$, and $a_{d2} = a_{d3} = 1$. The effective charge $Q$ is determined by the dielectric constant of the lattice $\epsilon_l$. In our previous work\cite{11} we used the value $\epsilon_l = 40$ that approximately corresponds to the undoped compound.\cite{22} This gave a reasonable fit of the NQR lines, but still the widths were about 20-30% larger compared to experiment. In the present paper, we fine tune the NQR widths by using $\epsilon_l$ as a fitting parameter. Our best fit yields

\[ \text{LSCO}: \quad \epsilon_l = 30(1 + 6.25p). \quad (10) \]

Thus the value of $\epsilon_l$ depends on doping, $\epsilon_l = 30$ for the undoped compound,\cite{22} and $\epsilon_l = 60$ for the optimally doped compound ($p = 0.16$). The coefficient 6.25 has been obtained by fitting the NQR widths, see below. It is natural to have some doping dependence of the lattice dielectric constant since the lattice dynamics may change locally (get softer) with La $\rightarrow$ Sr substitution. In our dimensionless units, the effective charge $Q$ is

\[ Q = \frac{e^2}{\epsilon_l a_0 J} \approx 30/\epsilon_l. \quad (11) \]

According to the same logic the Coulomb interaction between holons \cite{11} is replaced by

\[ U_{ij} \rightarrow Q \left( \frac{1}{\sqrt{|r_{i} - r_{j}|^2 + a_{HF}^2}} \right) \]

\[ + \sum_{n=1}^{\infty} \frac{2(-1)^n}{\sqrt{|r_{i} - r_{j}|^2 + (2nd)^2}} \].

The HF Hamiltonian is diagonalized in a $36 \times 36$ cluster. The resulting charge densities for particular realizations of Coulomb defects at different doping levels are shown in Fig. 3. To calculate the NQR spectrum of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The charge density of mobile holes in \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 calculated at zero temperature and different doping levels.}
\end{figure}

plane $^{63}\text{Cu}$, we first calculate the hole density distribution averaged over 20 random impurity configurations,
and then convert the hole density at a site \( i \) to the NQR frequency using the following scaling:

\[
\nu_i = 33 + 19 n_i \text{ (MHz)},
\]

(13)

which implies that the NQR spectrum is directly related to the charge density distribution. The resulting NQR spectra for zero temperature and for \( T = 600 \text{ K} \) are presented in Fig. 4. The theoretical NQR spectra at \( T = 600 \text{ K} \) agree very well with experimental data.

Although we are not aware of NQR data at low temperatures, the theoretical spectra at \( T = 0 \) are shown in order to demonstrate how the charge density distribution evolves with temperature. It is instructive to present the widths of the charge density distribution. Our simulation yields

\[
\text{LSCO at } p = 0.16 : \begin{cases} 
  \Gamma_p(T = 0) = 0.12 \\
  \Gamma_p(T = 600 \text{K}) = 0.09,
\end{cases}
\]

\[
\text{LSCO at } p = 0.08 : \begin{cases} 
  \Gamma_p(T = 0) = 0.07 \\
  \Gamma_p(T = 600 \text{K}) = 0.05. \quad (14)
\end{cases}
\]

In our previous work,\(^1\) we performed similar calculations for \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) and demonstrated that the Hartree-Fock calculation reproduces reasonably well the evolution of NQR lineshapes with doping. However, the calculated NQR linewidths were about 20-30\% larger compared to the experimental values. The goal of the present calculation is to fit the NQR linewidths quantitatively, using the dielectric constant\(^1\) as a fitting parameter. Based on this fit we accurately quantify the charge inhomogeneity and the hole mean free path as discussed below. We also note that the previous calculation\(^1\) has found an additional high frequency hump/shoulder in the NQR line. The hump was due to the strong Coulomb binding of holes to the accidently clustered Coulomb defects. The binding is very sensitive to the strength of the Coulomb attraction. This binding does not show up in the present calculation because of the larger value of the dielectric constant used, and also due to the fact that we impose here the "nonadjacent" condition for Coulomb defects [see the paragraph before Eq. (9)]. As suggested in Ref.\(^6\) the experimentally observed high frequency hump (the NQR "B-line") is most probably due to the direct action of Sr ion Coulomb potential on the Cu nucleus, which is beyond the scope of the present model.

B. \( \text{HgBa}_2\text{CuO}_{4+\delta} \)

Interstitial oxygen ions in \( \text{HgBa}_2\text{CuO}_{4+\delta} \) are located right between two neighboring \( \text{CuO}_2 \) layers, on top of four adjacent \( \text{Cu} \) sites.\(^1\) The minimal model for \( \text{HgBa}_2\text{CuO}_{4+\delta} \) is shown in Fig. 5. There is one layer of oxygen defects above the \( \text{CuO}_2 \) plane and another defect layer below it. Concentration of defects in each defect layer is \( \delta \). We assume that each interstitial oxygen donates two holes into the \( \text{CuO}_2 \) plane, i.e.,

\[
p = 2\delta. \quad (15)
\]
According to this picture, the holon interaction with a defect, Eq. (14) is replaced by
\[ U_{li} \rightarrow -2Q \left( \frac{1}{\sqrt{|R_i - r_i|^2 + a_d^2}} \right) \]
\[ + \sum_{n=1}^{\infty} \frac{(-1)^n}{\sqrt{|R_i - r_i|^2 + (2nd + d/2)^2}} \]
\[ + \sum_{n=1}^{\infty} \frac{(-1)^n}{\sqrt{|R_i - r_i|^2 + (2nd - d/2)^2}} \].

The interlayer distance in HgBa\(_2\)CuO\(_{4+\delta}\) is \( d = 2.5 \), and each interstitial oxygen carries "charge" \(-2Q\). Taking into account size of the Zhang-Rice singlet, we have \( a_d = \sqrt{a_{ZR}^2 + (d/2)^2} \approx 1.5 \). The hole-hole interaction has exactly the same form as that in La\(_{2-x}\)Sr\(_x\)CuO\(_4\), Eq. (12), with the interlayer distance \( d = 2.5 \) and with the value of \( Q \) described below. In each defect layer we simulate positions of the defects randomly, and impose again the nonadjacent condition for the defects.

Similar to the procedure in La\(_{2-x}\)Sr\(_x\)CuO\(_4\), we fine tune the NQR widths using the lattice dielectric constant \( \epsilon_l \) as fitting parameter. We find that in order to fit experimental NQR spectra \(^7,11\) the dielectric constant has to be taken as
\[ \epsilon_l = 30(1 + 25p) \] (17).

Note that the doping dependence of \( \epsilon_l \) in this case is four times stronger than that in Eq. (10). The stronger dependence is quite natural since it is due to the shift of the interstitial oxygen position in an applied electric field. The shift is significant because binding of interstitial oxygens in the lattice is weak. In other words, a dopant oxygen brings in new local phonon modes which enhance the dielectric constant. The effective charge \( Q \) is determined by the same Eq. (11), with \( \epsilon_l \) from Eq. (17).

The HF Hamiltonian is diagonalized in a 36 \( \times \) 36 cluster. The resulting charge densities for particular realizations of Coulomb defects at different doping levels are shown in Fig. 6. A strong charge inhomogeneity induced by oxygen dopants is apparent. However, density distribution profiles here are much smoother than in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) as one can easily see by comparing Figs. 6 and 2 at same doping levels.

Now, we address the NQR spectrum of the in-plane \(^{63}\)Cu in HgBa\(_2\)CuO\(_{4+\delta}\). We first calculate the hole density distribution averaged over 20 random impurity configurations, and then convert the hole density at a site \( i \) to the NQR frequency by
\[ \nu_i = C + 30n_i \text{ (MHz)} \] (18),
where \( C \) is a doping independent constant. Note that the coefficient 30 MHz in this formula is different from that in Eq. (13). We found the coefficient in Eq. (18) by fitting the NQR line centers using the experimental data of theoretical calculations of electric field gradients \(^{24}\). Since NQR data for HgBa\(_2\)CuO\(_{4+\delta}\) are taken at sufficiently low temperatures, we perform calculations only at \( T = 0 \). Fig. 7 shows the theoretical NQR lines by assuming \( C = 0 \), since it is an irrelevant constant shift. The calculations agree well with the experimental data.
of Refs. 7, 11. At optimal doping \( p = 0.16 \), the NQR linewidth in HgBa\(_2\)CuO\(_{4+\delta}\) is \( \Gamma_{NQR} \approx 2.6 \) MHz. The widths of the charge density distribution are

\[
\begin{align*}
HBCO \text{ at } p = 0.16 &: \quad \Gamma_p(T = 0) = 0.09 , \\
HBCO \text{ at } p = 0.08 &: \quad \Gamma_p(T = 0) = 0.08 .
\end{align*}
\]  

Comparing with the corresponding values for La\(_{2-x}\)Sr\(_x\)CuO\(_4\) in Eq. (14), we see that at zero temperature the amplitudes of charge inhomogeneities in HgBa\(_2\)CuO\(_{4+\delta}\) and in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) are quite similar. At optimal doping \( p = 0.16 \), the amplitude of charge inhomogeneity in HgBa\(_2\)CuO\(_{4+\delta}\) is only by 30\% smaller than that in La\(_{2-x}\)Sr\(_x\)CuO\(_4\).

C. Density of states and mean free path

A comparison between Eqs. (14) and (19) suggests that the hole density inhomogeneity in HgBa\(_2\)CuO\(_{4+\delta}\) is pretty close to that in La\(_{2-x}\)Sr\(_x\)CuO\(_4\). This seems rather surprising, given that the superconducting critical temperature in HgBa\(_2\)CuO\(_{4+\delta}\) is much higher than that in La\(_{2-x}\)Sr\(_x\)CuO\(_4\). Indeed, a disorder reduces the \( d\)-wave superconducting critical temperature and, based on this argument, one can expect that La\(_{2-x}\)Sr\(_x\)CuO\(_4\) is "more disordered". However, one should quantify exactly what is the measure of the disorder. While the overall amplitude of the charge inhomogeneity is one possible factor, the hole mean free path is another and in fact more important measure of the disorder. We already noticed that the spatial charge distribution profiles induced by interstitial oxygens and Sr-dopants are rather different. To quantify this difference in more detail, we calculate the quasiparticle DOS defined in the standard way

\[
\rho(\epsilon) = \frac{1}{N} \sum_n \delta(\epsilon - E_n) ,
\]

where \( N \) is the total number of sites, and \( E_n \) is the \( n\)-th eigenenergy. Plots of the DOS in HgBa\(_2\)CuO\(_{4+\delta}\) and in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) at doping \( p = 0.16 \) are shown in Figs. 8 and 9 together with the charge profiles for particular disorder realizations. The DOS has been obtained after averaging over 40 different disorder realizations. We have checked that the DOS calculated with 20 realizations of random dopant positions is practically the same as the DOS calculated with 40 realizations. This means that 40 realizations is sufficient to disregard the statistical noise. The calculated DOS exhibits pronounced oscillations. These oscillations are a byproduct of the finite size of the cluster. Maxima of the DOS correspond to degenerate states with dispersion (3) on the 36\times36 torus. The oscillations must certainly disappear in the thermodynamic limit. However, oscillations have a physical meaning: they indicate that the quantum states are quite extended, with the hole mean free path \( l \) comparable with the size of the cluster used. To estimate the

FIG. 8: (Color online) (a) Density of states and (b) charge density profile in HgBa\(_2\)CuO\(_{4+\delta}\) at optimal doping \( p = 0.16 \). Shown in the inset of panel (a) is the DOS of the homogeneous model with effective scattering rate \( \eta = 0.014 \).

FIG. 9: (Color online)(a) DOS and (b) charge density profile in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) at \( p = 0.16 \). The inset shows the DOS of the homogeneous model with scattering rate \( \eta = 0.021 \).
mean free path more accurately we use the following procedure. We consider the DOS of an ideal homogeneous system described by the Hamiltonian (2). It consists of \( \delta \)-functions whose positions are fixed by periodic boundary conditions. The weight of each \( \delta \)-function can be easily calculated for the 36\times36 torus. Now, we artificially broaden each \( \delta \)-function,

\[
\delta(\epsilon - \epsilon_n) \rightarrow \frac{1}{\pi} \frac{\eta}{(\epsilon - \epsilon_n)^2 + \eta^2},
\]

(21)
to simulate a disorder scattering. We find that the DOS of this model is very sensitive to \( \eta \). Then, we adjust the broadening \( \eta \) to reproduce (roughly) the amplitudes of the DOS oscillations obtained in our actual calculations, as shown in Figs. 8(a) and 9(a). This gives the following values of the effective broadening: \( \eta = 0.014 \) for HgBa\(_2\)CuO\(_{4.08}\), and \( \eta = 0.021 \) for La\(_{1.84}\)Sr\(_{0.16}\)CuO\(_4\).

The mean free path of a hole at the Fermi surface can be then estimated as:

\[
l = v_F \tau = \frac{v_F}{2\eta},
\]

(22)
where \( \tau = 1/2\eta \) is the collision time. At small doping, \( p \ll 1 \), the dispersion (3) results in the Fermi velocity \( v_F \approx 8\alpha_0 v_F \). Hence, at \( p = 0.16 \), the Fermi velocity is \( v_F \approx 1.4J_0 \). Together with the above values of \( \eta \), this results in the following estimates for the hole mean free paths:

\[
\begin{align*}
\text{HgBa}_2\text{CuO}_{4.08} & : l \approx 50a_0 \approx 19\text{nm}, \\
\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4 & : l \approx 34a_0 \approx 13\text{nm}.
\end{align*}
\]

(23)
We thus find that La\(_{2-x}\)Sr\(_x\)CuO\(_4\) is indeed more disordered, in the sense that it has a shorter mean free path. The different mean free paths are due to different distances from the CuO\(_2\) plane to the Coulomb defect (interstitial oxygen versus Sr-dopant), and due to different distances between Coulomb defects. In HgBa\(_2\)CuO\(_{4+\delta}\), both distances are larger, therefore the Coulomb potential is smoother and hence less contributes to the large angle scattering. This difference is clearly reflected in the charge density profiles shown in Fig. 8(b) and 9(b). Overall amplitudes of the charge inhomogeneity are pretty close, but the charge distribution in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) is much more spiky. This gives rise to the strong scattering with large momentum transfer which is detrimental for \( d \)-wave superconductivity.

Considering the superconducting correlation length \( \xi \approx 2 \) \( \text{nm} \), one finds that \( l/\xi \sim 6 \) in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) and \( l/\xi \sim 10 \) in HgBa\(_2\)CuO\(_{4+\delta}\). One should therefore expect that the disorder suppression of superconductivity in HgBa\(_2\)CuO\(_{4+\delta}\) is indeed weaker. In addition, according to our fits of the NQR data, the effective ionic dielectric constant \( \epsilon_l \) in HgBa\(_2\)CuO\(_{4+\delta}\), Eq. (17), is larger than that in La\(_{2-x}\)Sr\(_x\)CuO\(_4\), Eq. (19). At the optimal doping \( p = 0.16 \), for example, \( \epsilon_l (\text{LSCO}) = 60 \) and \( \epsilon_l (\text{HBCO}) = 150 \). The larger \( \epsilon_l \) in HgBa\(_2\)CuO\(_{4+\delta}\) implies better screening of the Coulomb repulsion between holes and hence a smaller Coulomb pseudopotential. This may further enhance \( T_c \) of HgBa\(_2\)CuO\(_{4+\delta}\) compared to that of La\(_{2-x}\)Sr\(_x\)CuO\(_4\).

### IV. Nanoscale Hole Density Inhomogeneity in the Surface Layer of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\)

Recent STM experiments\(^3\)\(^-\)\(^5\) have revealed large variations of pairing gaps in Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) which are spatially correlated with the dopant oxygen density. Motivated by this observation, we now consider the charge distribution in the surface CuO\(_2\) layer of this compound. Our purpose is to estimate the magnitude of the charge inhomogeneity induced by interstitial oxygen dopants, and see how the hole density profile is correlated with the position of these oxygens. In the present work, we do not calculate the local DOS and hence cannot address STM directly. Instead, we calculate the charge distribution similar to the previous sections, and show that the effect of interstitial oxygen on charge inhomogeneity is very significant.

As we have seen above, charge distribution profiles depend on the lattice dielectric constant whose values can be reliably obtained by fitting the NQR data. Due to lack of systematic NQR data, we cannot determine the dielectric constant of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) in this way. Instead, we assume that the doping dependence of the lattice dielectric constant in the bulk of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) is described by the same formula Eq. (17) as in HgBa\(_2\)CuO\(_{4+\delta}\). This is because both compounds are doped by interstitial oxygens which have similar influence on lattice dynamics and dielectric screening. This adoption certainly ignores lattice structure details and should be further refined when NQR data is available. Nevertheless, we found that our results for Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) are fairly robust within a sensible variations of the dielectric constant, and thus they should give a qualitative description of the surface charge inhomogeneity.

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**FIG. 10:** (Color online) The Hartree-Fock model for Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) surface. Blue dots indicate the interstitial oxygen dopants. Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) is a double layer compound and a
schematic picture of the two surface CuO$_2$ layers is shown in Fig. 10. Interstitial oxygens are assumed to be located at $\lambda \approx 0.37$ nm above the CuO$_2$ layer, which is shown to be the most energetically favorable position. We assume that the surface concentration of Coulomb defects (interstitial oxygens) is $\delta$. They are randomly distributed and, similarly to the previous considerations, we impose again the condition that the defects never sit next to each other, i.e., the distance between the defects is always larger than $\sqrt{2}$ (in units of $a_0$). The separation between the CuO$_2$ layers in the double layer structure is $d = 0.33$ nm$\approx 0.86$. We treat the top layer by Hartree-Fock approximation, and the underneath layer as a “metallic” sheet that provides screening. There are also Coulomb defects underneath of the screening layer, but they are well screened by the metallic sheet and hence do not influence the Hartree-Fock procedure. The hole-defect and the hole-hole interaction in the Hartree-Fock top layer are of the following form:

$$U_{li} \rightarrow -2Q \left( \frac{1}{\sqrt{|R_i - r_i|^2 + a_d^2}} \right) \left( \frac{1}{\sqrt{|R_i - r_i|^2 + (2d + \lambda)^2}} \right)$$

$$U_{ij} \rightarrow Q \left( \frac{1}{\sqrt{|r_i - r_j|^2 + a_{HF}^2}} \right) \left( \frac{1}{\sqrt{|r_i - r_j|^2 + (2d)^2}} \right) .$$ (24)

Here $a_d = \sqrt{\lambda^2 + a_{ZR}^2} \approx 1.28$, and $a_{HF} = \sqrt{2a_{ZR}^2} \approx 1$. Note that there is only one image charge per physical charge because there is only one screening layer. We assume that the lattice contribution to the dielectric constant in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ has the form Eq. (17). On the surface, the dielectric constant is expected to be reduced to half of its value in the bulk, therefore

$$\epsilon^{BSCCO} = 15(1 + 25p),$$ (25)

and the value of effective “charge” $Q$ follows from Eq. (11).

Plots of the in-plane hole density for $\delta = 0.04$ ($p = 0.08$) and $\delta = 0.08$ ($p = 0.16$) are presented in Fig. 11 together with corresponding maps for these particular realizations of Coulomb defects. The plots demonstrate a large spatial variations in hole density. For the $\delta = 0.04$ case, the range of hole density modulation is about $0.03 < n_i < 0.15$, which is a very significant fluctuation, having in mind that the average hole density is $\langle n_i \rangle = p = 0.08$. The same strong inhomogeneity is seen in the $\delta = 0.08$ case, where the local density varies in the range roughly $0.10 < n_i < 0.23$, while average density is $\langle n_i \rangle = p = 0.16$. The density distribution curves for different doping levels are shown in Fig. 12.

We stress that the precise density profiles depend on the dielectric constant which, due to lack of NQR data for Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, is taken here in an ad hoc way. On a qualitative level, however, the density inhomogeneity is rather stable with respect to the value of the dielectric constant. For example, the widths of the surface density distributions plotted in Fig. 12 are only slightly larger than those obtained in the case of HgBa$_2$CuO$_{4+\delta}$, see Eq. (19). This is in spite of the fact that the results for HgBa$_2$CuO$_{4+\delta}$ have been obtained at the twice larger value of the dielectric constant. Therefore, we believe that our conclusion about the strong surface charge density inhomogeneity is very reliable.

Naturally, the charge density of mobile holes is higher around areas with higher interstitial oxygen concentration. Fig. 11 clearly shows this correlation. To quantify this, we define a correlation function between local hole density and dopant oxygen positions, which is analogous to the correlator introduced in Ref. 2 for analysis of the spatial variations of the local DOS. On a discrete lattice, the hole density $n_{ij}$ is defined on sites of the square lattice representing the CuO$_2$ plane. The function $f_{i}$ indicates

FIG. 11: (Color online) (a,d) The zero temperature hole density plots and (b,e) the hole density maps for the surface layer of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ for the average hole density $p = 0.08$ (left panels) and 0.16 (right panels). The lower panels (c) and (f) show positions of the oxygen dopants for the corresponding realizations of disorder. It is evident that the dopant oxygens locally increase the hole density.
the location of interstitial oxygens:

\[ f_i = \begin{cases} 
1 & \text{if } i \in \text{dopant oxygen}, \\
0 & \text{elsewhere}, 
\end{cases} \]

where \( i \) runs through points at the center of the plaquettes. The density-oxygen correlation function is then defined as

\[ C_{nf}(R) = \frac{1}{N} \sum_i \frac{[f_i - \bar{f}] [n_{i+R} - \bar{n}]}{\sqrt{A_fA_n}}, \]

with proper normalizations

\[
A_f = \frac{1}{N} \sum_i (f_i - \bar{f})^2, \quad A_n = \frac{1}{N} \sum_j (n_j - \bar{n})^2,
\]

where \( \bar{f} = \frac{1}{N} \sum f_i = \delta \) and \( \bar{n} = \frac{1}{N} \sum n_j = p \). Fig. 13 shows the correlation function \( C_{nf}(R) \) averaged over 20 disorder realizations for each doping. There is a clear positive correlation due to the Coulomb attraction to the oxygen defects. The value of the correlator at \( R \to 0 \) is \( C \approx 0.3 - 0.4 \) and the scale at which it goes to zero is about 10-15 Å. Interestingly, the correlator between the gap in local DOS and the interstitial oxygen position measured in STM shows the same positive correlation with very similar scales. Further investigation is necessary to clarify if there is a connection between these two correlators, and to understand the physical reasons behind this apparent correspondence.

\[ \text{FIG. 12} \text{ (Color online) The zero temperature hole density distribution in the surface layer of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ at various doping levels } p. \text{ Each curve is averaged over 20 realizations of disorder.} \]

In this paper, we study the spatial distribution of doped holes in cuprates, focusing particularly on a comparison between two different physical situations: doping by a cationic substitution Sr for La as in La$_{2-x}$Sr$_x$CuO$_4$, and doping by interstitial oxygen ions as in HgBa$_2$CuO$_{4+\delta}$. The main results are summarized as follows.

The hole density inhomogeneity in HgBa$_2$CuO$_{4+\delta}$ is nearly as strong as in La$_{2-x}$Sr$_x$CuO$_4$. For example, at the optimal doping \( p = 0.16 \) the width of the charge density distribution is about \( \Gamma_p = 0.09 \), which is close to the corresponding number \( \Gamma_p = 0.12 \) in La$_{2-x}$Sr$_x$CuO$_4$. This conclusion is well supported by the comparison of our calculations with the existing NQR data in HgBa$_2$CuO$_{4+\delta}$ and La$_{2-x}$Sr$_x$CuO$_4$. In spite of the close overall amplitudes, the landscape of charge inhomogeneity in these two compounds are very different. In oxygen doped HgBa$_2$CuO$_{4+\delta}$, the disorder potential profiles are much smoother than that in Sr-doped La$_{2-x}$Sr$_x$CuO$_4$. Correspondingly, the hole mean free path in HgBa$_2$CuO$_{4+\delta}$ is larger. In other words, disorder induced scattering processes with a large momentum transfer (which are destructive for \( d \)-wave pairing) are less pronounced in oxygen doped HgBa$_2$CuO$_{4+\delta}$ compared to the case of La$_{2-x}$Sr$_x$CuO$_4$. In addition, the screening of the Coulomb repulsion between holes in HgBa$_2$CuO$_{4+\delta}$ is about twice stronger than that in La$_{2-x}$Sr$_x$CuO$_4$. In our opinion, these two reasons might explain the much higher superconducting critical temperature of oxygen doped HgBa$_2$CuO$_{4+\delta}$.

We found that the charge density nanoscale inhomogeneity in the surface CuO$_2$ layer of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (the layer available for STM) is of the same magnitude as that in the bulk of HgBa$_2$CuO$_{4+\delta}$. As expected on physical grounds, the hole density positively correlates with the positions of interstitial dopant oxygen. Remarkably, the correlation function obtained here resembles the pos-
itive correlation between the local gap and dopant oxy-
gens seen in the STM data. The reason for this appar-
ent coincidence and implications of the charge inho-
ogeneity for the spatial variations of the pairing gaps in 
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ have to be clarified in future studies.

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