ing level in YBCO. Our choice seems reasonably consistent with these experiments.

The potentials in (3) and (4) are calculated from a self-consistent mean-field treatment. We write

$$\Phi_i = \begin{cases} \phi_i + \epsilon_p, & i \in \text{plane} \\ \phi_i + \epsilon_c, & i \in \text{chain} \end{cases} \quad (7)$$

where ϕ_i is the electrostatic potential, and $\epsilon_{c(p)}$ includes the chemical potential and the energy of the chain (plane) tight binding orbitals. We determine ϵ_p and ϵ_c by specifying the bulk plane and chain charge densities at optimal doping ($\delta = 0.08$), which we take to be $n_p = 0.84$ and $n_c = 0.48$ electrons per 2D unit cell respectively. Note that, once n_p is chosen, n_c is set by the constraint of charge neutrality, given by Eq. (11) below. Our self-consistent calculations then find $\epsilon_c - \epsilon_p = 3.176$ eV at optimal doping. We assume that the tight binding orbitals are not modified by doping, so that $\epsilon_c - \epsilon_p$ is held constant througout this work. In our calculations chemical doping modifies the band structure only through the electrostatic potential ϕ_i.

The Coulomb potential ϕ_i is then calculated self-consistently within the Hartree approximation, under the assumption that the charge is uniformly distributed within each layer. For the planar geometry shown in Fig. 1,

$$\phi_i = \begin{cases} -\kappa \sum_j \sigma_j |z_i - z_j| + U \frac{n_i}{2}, & i \in \text{plane} \\ -\kappa \sum_j \sigma_j |z_i - z_j|, & i \in \text{chain} \end{cases} \quad (8)$$

where the $Y_{1-y}Ca_y$ layers are implicitly included in the sum over j and

$$\kappa = \frac{2\pi e^2 d_z}{\epsilon a_0^2}. \quad (9)$$

In (8), U is the intraorbital Coulomb potential for the CuO_2 layers, which we take to be 4 eV. The total 2D charge density in layer i is $\sigma_i = Z_i - n_i$, where Z_i is the charge density of the ionic cores. Here, n_i is measured relative to the Cu^{3+} and O^{2-} states, so that

$$\sigma_j = \begin{cases} 1 + 2\delta - n_j, & j \in CuO_{1-\delta} \text{ chain} \\ -1 - n_i, & j \in CuO_2 \text{ plane} \\ 3 - y, & j \in Y_{1-y}^{3+}Ca_y^{2+} \text{ layer} \end{cases} \quad (10)$$

All charge densities are in units of e/a_0^2, where $a_0 \approx 4$ Å is the 2D lattice constant. Electrical neutrality requires that

$$n_c + 2n_p = 2 + 2\delta - y. \quad (11)$$

In Eq. (8), z_i is the z-coordinate of layer i, in units of the c-axis lattice constant $d_z \approx 12$ Å. Within a unit cell, the layers are at $z = 0$ (chain), $z = 0.354$ (first plane), $z = 0.5$ (Y layer), and $z = 0.646$ (second plane).[36] The weak doping dependence of these values is ignored here. The dielectric constant ϵ in (8) is not well known, but is

TABLE I: Parameters for the tight binding model for YBCO.

Parameter	Value
t_p	105 meV
t'	-0.277
t''	0.234
t'''	-0.042
t_c	500 meV
$t_{\perp p}$	61 meV
$t_{\perp c}$	$1.1 t_{\perp p}$

believed to be around $\epsilon = 20$, which is the value taken here.

For a given potential Φ_i, the charge density in layer i is found from the eigenvalues $E_{\alpha,\mathbf{k}}$ and eigenstates $\Psi_{\alpha,\mathbf{k}}(i,\sigma)$ of $H_{\mathbf{k}}$ via

$$n_i = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{\alpha=1}^{2N} |\Psi_{\alpha,\mathbf{k}}(i,\uparrow)|^2 f(E_{\alpha,\mathbf{k}}) \quad (12)$$

where $f(x)$ is the Fermi function, the factor of 2 is for spin, and N_k is the number of k-points in the sum. The band index α ranges from 1 to $2N$ because the number of bands in the film is equal to twice (including spin) the number of conducting layers. The updated charge density is used to re-calculate Φ_i, which is then used in the next iteration for n_i. The iterations proceed until the difference between n_i in two consecutive iterations is less than 10^{-5}. To reduce the computational workload, Φ_i is calculated in the normal state.

We finish this section with a brief discussion of the fitting procedure used to get the model parameters shown in Table I. As discussed above, we fit the 2D dispersions for the CuO_2 layers to the surface states measured in Ref. 19. In order to avoid complications from the chains, we fit the energy spectrum for an isolated CuO_2 bilayer to the measured bands in regions of the Brillouin zone far from the chain Fermi surface. The model bilayer has bonding and antibonding bands, with energies $\xi^{\pm}(\mathbf{k}) = \xi_p(\mathbf{k}) \pm t_{\perp p}$, which allows us to determine t_p, t', t'', t''', and $t_{\perp p}$. One potential difficulty with this fitting process is that it assumes that the electrostatic potential is the same in the top two CuO_2 layers, meaning that we attribute the experimental bilayer splitting entirely to $t_{\perp p}$. If we allow for a potential difference $\Delta\phi$ between the CuO_2 layers making up the bilayer (due to band bending at the surfaces), then $\xi^{\pm}(\mathbf{k}) = \xi_p(\mathbf{k}) \pm \sqrt{(\Delta\phi/2)^2 + t_{\perp p}^2}$. Self-consistent calculations reported in the next section suggest $\Delta\phi \sim 10$ meV while the measured $t_{\perp p} \approx 60$ meV; it follows that $\Delta\phi$ modifies the band energies by less than 1% and can safely be neglected.

There are, at present, no reliable measurements of the chain band structure. We therefore assume that strong correlations are not significant in the CuO chains (which are roughly quarter-filled), and that the chain bandwidth