Revealing Symmetry-broken Superconducting Configurations by Density Functional Theory

Zi-Kui Liu and Shun-Li Shang

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Abstract

A coherent theory for both conventional and unconventional superconductors is currently lacking. Here we show that the electron charge densities of Al, YBa₂Cu₃O₇ (YBCO), and LaH₁₀ along with Pb and Nb₃Sn share the same feature of electron charge gains in their respective superconducting configurations (SCCs) predicted by first-principles calculations based on the density functional theory (DFT). It is discovered that the formation of SCCs is due to the local symmetry breaking from their normal conducting configurations (NCCs), and the electron charge gains in SCCs form electron tunnels in crystals that resemble pontoons, thus termed as electron pontoon tunnel (EPT) here. The nuclei promoting the formation of EPTs in conventional superconductors have strong bonding with other nuclei, resulting in their EPTs easily destroyed and thus low superconducting critical temperature (T_c), while in unconventional superconductor, this bonding is very weak as shown by negative stretching force constants in YBCO, thus resulting in much higher T_c . The fundamental understanding of SCCs and the capability to predict them by DFT enable theoretical search of room temperature superconductors without empirical models.

1 Main text

Superconductivity is a phenomenon discovered in 1911 by Kamerlingh Onnes (1) where electrical resistance of mercury vanishes at temperatures below a critical temperature (T_c) of 4.2 K. The Bardeen-Cooper-Schrieffer (BCS) theory (2, 3) was developed in 1957 as a microscopic theory of superconductivity in terms of the condensation of Cooper pairs. It was postulated that this paired state of electrons originates from the electron-phonon interaction and has a lower energy than the Fermi energy and can migrate freely in the system. Due to the weak pairing interaction ($\sim 10^{-3} eV$), thermal energy can easily break the pairs, resulting in conventional superconductors with low T_c .

Since the BCS theory, one of the important milestones in superconductivity was the discovery of superconductors with T_c above the commonly believed limit of 30 K based on the BCS theory, initially at 35 K for CuBa_{0.15}La_{1.85}O₄ (4) and soon reached 80 to 93 K for (Y_{0.6}Ba_{0.4})₂CuO_{4- δ} (5). The highest T_c superconductors under ambient pressure were HgBa₂Ca₂Cu₃O_{8+ δ} in the range of 133–138 K with T1 substitution of Hg (6, 7). Under high pressures, higher T_c superconductors were reported more recently among various hydrogen containing compounds under high pressure such as 250 K under 170 GPa for LaH₁₀ (8). The latest report was on the global room-temperature one-dimensional superconductivity at 300 K observed in the cleaved highly oriented pyrolytic graphite carrying dense arrays of nearly parallel surface line defects (9).

One major theoretical breakthrough in physics since the BCS theory is the density function theory (DFT) (10, 11) as a solution to the many-body Schrödinger equation in quantum mechanics. DFT articulates that for a given system, there exists a ground-state configuration (GSC) at 0 K and 0

GPa that its energy is at its minimum value with a universal functional of the interacting electron gas density (10). This unique ground-state electron density is obtained by explicitly separating the independent-electron kinetic energy and long-range Coulomb interaction energy and replacing the many-body electron problem using independent valence electrons with an exchange-correlation functional of the electron density and an associated exchange-correlation energy (11). DFT plays a central role in the prediction of T_c , either based on the Eliashberg equation with model parameters or explored fully from first-principles for superconductors (SCDFT) or beyond with nonadiabatic effects (12).

However, the outmost fundamental challenge in DFT is to predict the superconducting configurations (SCCs) and the normal conducting configurations (NCCs) as a function of pressure at 0 K. It was postulated (13) that the statistical competition among the SCCs and NCCs can then be used to predict T_c in terms of a recently termed zentropy theory (14). In DFT, both the electron-electron and electron-phonon interactions are treated indirectly through their contributions to and interactions with the overall potential of the system. Thus, DFT cannot directly simulate the Cooper pairs which require an explicit description of those interactions. On the other hand, it is important to realize that DFT formulated by Hohenberg and Kohn (10) is an exact theory of manybody systems. It is thus self-evident that DFT should be able to differentiate the electron densities of SCCs and NCCs as discovered in the present work. An approach was developed by Lüders et al. (15) for the description of superconductors in thermal equilibrium within a formally exact density functional framework and applied to the prediction of T_c of pure elements by Marques et al. (16). However, it does not explicitly differentiate SCC and NCC at 0 K.

It is noted that the key discovery in the recently developed strongly constrained and appropriately normed (SCAN) meta-generalized-gradient approximation (meta-GGA) of electron density functional (17-20) is that the strong correlations within a symmetry-unbroken ground-state wavefunction can show up in approximate DFT as symmetry-broken spin densities or total densities due to soft modes of fluctuations such as spin-density or charge-density waves at nonzero wavevector. Consequently, an approximate density functional for exchange and correlation with symmetry breaking, though less accurate than an exact functional, can be more revealing with its utility demonstrated for a number of cases (19-21). This inspired the present authors to search for the SCCs as symmetry-broken configurations of its NCC.

The best system to test our postulations of superconductivity (13) and search for SCCs is pure Al with its temperature-pressure (T-P) superconducting phase diagram shown in Fig. 1. T_c of Al is about 1.18 K at 0 GPa and reduces to 0.075 K at 6.2 GPa (22). In searching for the symmetry-broken SCCs of face-centered cubic (fcc) NCC Al, we built a 32-atom 2×2×2 supercell and randomly introduced perturbation of 0.015Å to the nuclei positions to break the symmetry with details presented in the method section. It was found that the perturbations on every other (001) layer resulted in stable configurations, and four symmetry-broken SCCs was discovered with their energies lower than that of the symmetry-unbroken NCC Al. The standard deviations (SD) of nuclei displacements in SCCs with respect to those in NCC of Al together with their energy differences (ΔE) are plotted in Fig. 2 as a function of volume and pressure. The transition between the SCCs and NCC is around 15.6 ± 0.2 Å³/atom (or 5.0 ± 1.0 GPa) in reasonable agreement with the critical pressure (P_c) of the superconductivity extrapolated to 0 K as shown in Fig. 1 (i.e., $P_c \sim 6.5$ GPa). The phonon dispersions of one of four SCCs (SCC1) and NCC of Al at external

pressure of 2.8 GPa are plotted in the supplementary Fig. S 1 for both the 1-atom and 32-atom supercells. It shows that the dispersion curves of SCC1 are disturbed with respect to those of NCC due to symmetry-breaking, making some degenerate curves separated, such as the acoustic branches from Γ to R. It is worth mentioning that phonon densities of states for both SCC and NCC are almost equivalent as shown in Fig. S 1(e), resulting in nearly identical zero-point energy and entropy contribution to free energy.

Fig. 1: Temperature-pressure (T-P) superconducting phase diagrams of Al (22).

Fig. 2: DFT-based calculations of fcc Al: (a) relative total energy (E) of SCCs and NCC, (b) energy difference (ΔE) between SCCs and NCC, and (c) standard deviations (SD or σ) of nuclei fluctuation in SCCs with respect to NCC, as a function of volume and pressure.

The differential charge densities of SCC1 and NCC of Al in terms of electron gains with respect to their free electrons are plotted in Fig. 3(a) and (b), showing nonsymmetric and symmetric patterns, respectively. Their difference is plotted in Fig. 3 (c) to depict the electron gains in SSC1 with respect to NCC with a tunnel-like geometry along the [101] direction. Their movies are shown in supplementary materials. As it will become evident in YBa₂Cu₃O₇ (YBCO), we term these tunnels as electron pontoon tunnel (EPT). It is postulated that these EPTs provide pathways for electron transport without resistance, resulting in superconductivity in Al at 0 K and 0 GPa.

Similarly to fcc Al, symmetry-breaking promotes the formation of EPT in Pb and Nb₃Sn as shown in supplementary Fig. S 2, Fig. S 3, and Fig. S 4, respectively.

Fig. 3: Differential charge density of fcc Al in terms of the 32-atom supercell viewed along the [010] b-

axis direction regarding electron gains at 2.8 GPa for (a) SCC1 and (b) NCC with respect to free electrons using the same isosurface level $\Delta \rho = 1.7 \cdot 10^{-3}$ electrons/Å³; and (c) the difference of (a) and (b) using $\Delta \rho = 8.5 \cdot 10^{-5}$ electrons/Å³, indicating the formation of electron pontoon tunnels (EPT) along

[101]. Their movies are included in the supplementary materials.

To predict T_C of fcc Al at 0 GPa, we use our zentropy theory (13, 14) that represents the total entropy of a system with *m* configurations as follows

$$S = \sum_{k=1}^{m} p^{k} S^{k} - k_{B} \sum_{k=1}^{m} p^{k} ln p^{k}$$
 Eq. 1

where p^k and S^k are the probability and entropy of configuration k, respectively, and k_B the Boltzmann constant. Eq. 1 gives the revised statistical mechanics as follows

$$Z = e^{-\frac{F}{k_B T}} = \sum_{k=1}^{m} Z^k = \sum_{k=1}^{m} e^{-\frac{F^k}{k_B T}}$$
 Eq. 2

$$p^{k} = \frac{Z^{k}}{Z} = e^{-\frac{F^{k}-F}{k_{B}T}}$$
 Eq. 3

where Z, F, Z^k , and F^k are the partition functions and Helmholtz energies of the system and the configuration k, respectively, and T is the temperature. The zentropy statistical mechanics uses F^k instead of total energy in standard statistical mechanics due to non-zero S^k in Eq. 1 for SCCs and NCCs. The predicted p^k values and their first derivatives (D1) of two SCCs (SCC1 and SCC2) of fcc Al are plotted in Fig. 4(a) as a function of temperature using the fitted properties 0 K by equation of state (EOS) at 0 K, see supplementary Table S 1, and phonon-based quasiharmonic approximation. Using the inflection point of p^k as a criterion of superconducting transition, the

zentropy theory predicts $T_c = 1.9 \pm 1.1$ K at 0 GPa, where the standard deviation 1.1 is due to the uncertainty of properties in Table S 1. The predicted T_c is in good agreement with experimental observations around 1.18 K (22), and more work is needed to reduce the uncertainty of zentropy prediction through larger supercells and more configurations. Other properties related to the second derivatives of free energies can also be predicted such as heat capacity shown in Fig. 4(b) (13, 14).

Fig. 4: Zentropy theory for two fcc Al SCCs. (a) Predicted probability (p^k) and its first derivative (D1) as a function of temperature under 0 GPa. The inflection point is one of the definitions to determine T_C between superconducting and normal conducting states of which both are mixture of SCCs and NCC. The zentropy theory predicts $T_C = 1.9 \pm 1.1$ K at 0 GPa. (b) Predicted heat capacity at constant volume (C_V) based on configurational entropy S_{conf} .

Now let us examine the typical unconventional superconductor YBCO with its fully relaxed $2\times2\times1$ supercell shown in Fig. 5(a) and the properties by EOS fitting in Table S 2. It can be seen that the Cu1-O1 plane is flat, while the Cu-O2-Cu-O3 plane is wavy. The stretching force constants (SFCs) (*23*) are plotted in Fig. 5(b) showing that the SFC between Cu1-O4 is the largest, followed by those of Cu2-O2, Cu2-O3, and Cu1-O1. Bonding strengths represented by these SFCs (*23*) indicate two frames in YBCO with the frame 1 being the Cu1-O4-Ba-O1 structure and the frame 2 being the Cu2-O2-O3-Y structure. The SFCs within both frames are large (> 3 eV/Å²), while the SFCs between them are small (< 1 eV/Å²), particularly the SFC of Cu2-O4 is negative (-1.6 eV/Å²), and the SFCs of Ba-O2 and Ba-O3 are also negative (-0.5 eV/Å²) with a long bond length about 3 Å. It is further noted that the SFCs of Y-O2 and Y-O3 (< 0.9 eV/Å²) are much smaller than those of

Cu2-O2 and Cu2-O3 (> 4 eV/Å²). The crystallographic information presented in Table 1 depicts that the rigid frame 1 is symmetry-unbreaking with Cu1-O1 on the same x and z levels and Cu1-O4 on the same x and y levels, while the wavy frame 2 is symmetry-breaking with O2-O3 on the same z level and Cu2 shifting towards the frame 1 and Y loosely connecting the two O2-Cu-O3 layers. The frame 2 structure in the middle of Fig. 5(a) thus resembles a three-layer pontoon structure floating between the two rigid frame 1 structures, thus the term EPT defined above and depicted by the differential charge density in terms of electron gains in Fig. 5(c) with its movie shown in supplementary materials.

Fig. 5: (a) Relaxed structure of the 52-atom 2×2×1 YBCO supercell with the bonds connecting key interactions indicted by the stretching force constants in (b) from phonon calculations and crystallographic information in Table 1, and (c) Differential charge gains (by yellow) in one of the O2-Cu2-O3 layers with isosurface level Δρ being 1/24 of the maximum density (0.0102 electrons/Å³), showing the charge connections, i.e., EPTs, along the Cu2-O2 and Cu2-O3 bonds.

Table 1: Crystallographic information of YBCO by experiments at 297 K according to X-ray and neutron powder diffractions (24) and DFT-based calculations by r²SCAN, including space group (SG), lattice parameters a, b, and c (in Å), and atomic positions x, y, and z.

Now let us exam LaH₁₀, a high T_c superconductor under high pressures (8). Fig. 6 shows the isosurface plots of differential charge gains of LaH₁₀ under external pressures of 0, 120, 180, and 210 GPa, respectively. With increasing pressure, charge gains around H atoms become more and more connected from the isolated states at low pressures, with the critical pressure about 170 GPa

(see the connected charge gains at 180 GPa under the current isosurface level of $\Delta \rho$), matching well with the experimental observation of critical pressure (8), and indicating the formation of EPT promoted by pressure in LaH₁₀. Their movies are shown in supplementary materials.

Fig. 6: Differential charge gains (by yellow) of LaH₁₀ at different pressures of (a) 0 GPa, (b) 120 GPa,
(c) 180 GPa, and (d) 210 GPa, with the isosurface level Δρ being 1/7 of the maximum charge density
(i.e., 0.0096, 0.0117, 0.0125, and 0.0126 electrons/Å³, respectively).

It can thus be concluded that the mechanism of superconductivity in both conventional and unconventional superconductors is the same and is originated from the formation of EPT due to symmetry-breaking displacements of some nuclei, which can be revealed by DFT. In conventional superconductors, EPT is tightly connected with the rest of the lattice and thus easily destroyed at low temperature due to lattice vibration. While in unconventional superconductors, EPT is weakly linked to the lattice structure and can thus sustain to much higher temperature. Therefore, a systematic search of higher T_c superconductors can be performed through tailoring the bond strengths in the frame 2 in YBCO and/or by a high-throughput combinatoric search of SCCs of other materials guided by artificial intelligence surrogate models trained on metaGAA of r^2 SCAN datasets and validated by DFT-based calculations.

2 Methods

The present works were performed by DFT-based first-principles calculations using the VASP code (25). The ion-electron interaction was described by the projector augmented wave (PAW) method (26) and the exchange-correlation (X-C) functional was depicted by the generalized

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gradient approximation (GGA) developed by Perdew, Burke, and Ernzerhof (PBE) (27) for Al, LaH₁₀, Pb, and Nb₃Sn and by the metaGAA of r^2 SCAN (28) for YBCO. In VASP calculations, electron configurations for each element were the same as those used by the Materials Project (29), and the energy convergence criterion of the electronic self-consistency was at least 10⁻⁶ eV/atom for all calculations with the other details shown in Table 2. Phonon calculations were performed using the supercell approach (30) in terms of the YPHON code (31). Here, the VASP code was again the computational engine to calculate force constants using the finite differences method. The employed supercell, the corresponding *k*-point meshes, and the other settings are the same as the aforementioned structural relaxations in Table 2.

 Table 2. Details used for DFT-based calculations for four superconductors, including their structures,

 supercell sizes, and X-C functionals, smearing method to determine partial occupancies for each orbital,

 k-point meshes, and energy cutoff (Ecut) for the plane-wave basis set. Their VASP POSCAR files are

 included in the supplementary materials.

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Fig. 1





Fig. 2



(a)



(b)



Fig. 3.





(a)





Fig. 5.



(a)



(b)



(c)



(d)

Fig. 6

Table	1.

Atom	<i>Expt.</i> (24)			<i>Calc. (This work by r²SCAN)</i>		
(or SG)	x (or a)	<i>y</i> (or b)	z (or c)	<i>x</i> (or a)	y (or b)	z (or c)
Pmmm	3.8203	3.8855	11.6835	3.8194	3.8712	11.7124
Ba	0.5	0.5	0.1839	0.5	0.5	0.1813
Y	0.5	0.5	0.5	0.5	0.5	0.5
Cul	0	0	0	0	0	0
Cu2	0	0	0.3550	0	0	0.3590
OI^*	0	0.5	0	0	0.5	0
<i>O2</i>	0.5	0	0.3782	0.5	0	0.3789
<i>O3</i>	0	0.5	0.3769	0	0.5	0.3786
04	0	0	0.1584	0	0	0.1584

*Occupancy of 0.910 by experiments.

^a Measured on a monocrystal YBCO using high-pressure XRD, need to read again these two

papers (32) and its ref. 2.

Table 2

Material	Structure	Supercell	X-C	Smearing ^a	k-point ^c	Ecut (eV)
Al	fcc	32-atom 2×2×2	GGA-PBE	1 (-5) ^b	30 (40) ^b	300 (450) ^b
Nb ₃ Sn	A15	8-atom 1×1×1	GGA-PBE	1 (-5) ^b	45 (55) ^b	301 (450) ^b
LaH ₁₀	$Fm\overline{3}m$	44-atom 1×1×1	GGA-PBE	1 (-5) ^b	15×15×15	400 (400) ^b
	(33)					
YBCO	Pmmm	52-atom 2×2×1	r ² SCAN	1 (-5) ^b	25 (35) ^b	400 (520) ^b
	(24)					

^a The same as those used in VASP, 1 indicates the Methfessel-Paxton technique (*34*) used for structural relaxations and phonon calculations, and -5 the tetrahedron method with a Blöchl correction (*35*) used to calculate change density.

^b The values in parentheses used to calculate change density when available.

^c Automatic *k*-point meshes were generated except for LaH₁₀.

Supplementary Materials

Following movies and POSCAR Files are available at <u>https://zenodo.org/doi/10.5281/zenodo.10900758</u>

- Movies
 - Differential charge density of SCC1 in terms of electron gains in Fig. 3(a): AL-SCC1(strE).mp4
 - Differential charge density of NCC in terms of electron gains in Fig. 3 (b): AL-NCC(fcc).mp4
 - Difference of differential charge density of SCC1 with respect to NCC in terms of electron gains in Fig. 3 (c): AL-SCC1-vs-NCC(E_fcc).mp4.
 - Differential charge density of YBCO in terms of electron gains in Fig. 5 (c): YBCO-short.mp4.
- POSCAR files with details in Table S 3.
 - POSCAR_AL_NCC_2.6GPa
 - POSCAR_AL_SCC1_2.6GPa
 - POSCAR_AL_SCC2_2.6GPa
 - o POSCAR_AL_SCC3_2.6GPa
 - o POSCAR_AL_SCC4_2.6GPa
 - o POSCAR_Nb3Sn_NCC_14.4GPa
 - o POSCAR_Nb3Sn_SCC1_14.4GPa
 - POSCAR_Nb3Sn_SCC2_14.4GPa
 - o POSCAR_Nb3Sn_SCC3_14.4GPa
 - POSCAR_YBCO_R2SCAN_0.1GPa





Fig. S 1: Phonon dispersions of fcc Al along high symmetry points of NCC and SCC1 at 2.8 GPa. (a) and (c) are for the 1-atom primitive cell, and (b) and (d) for 32-atom supercell, and (e) phonon density of states of SCC1, SCC2, and NCC.







Fig. S 2: DFT-based calculations of Nb₃Sn: (a) energy difference (ΔE) between SCCs and NCC, and (b) standard deviations (SD or σ) of nuclei fluctuation in SCCs with respect to NCC, as a function of volume

and pressure.







Fig. S 3: Differential charge density of Nb₃Sn in terms of the 8-atom supercell viewed along c-axis direction regarding electron gains for (a) one of the SCCs and (b) NCC with respect to free electrons using the same isosurface level $\Delta \rho = 0.0062$ electrons/Å³, and (c) difference of (a) and (b) using $\Delta \rho =$ 0.0013 electrons/Å³.







Fig. S 4: DFT-based calculations of Pb: (a) energy difference (ΔE) between SCCs and NCC, and (b) standard deviations (SD or σ) of nuclei fluctuation in SCCs with respect to NCC, as a function of volume and pressure.

Table S 1: Fitted properties at 0 K of fcc Al NCC and SCCs using the Birch-Morhaham EOS (36), including equilibrium volume (V_0), relative total energy (ΔE_0), bulk modulus (B_0) and its derivative with respect to pressure (B'). The average (AV) values and their standard derivations (SDs) of SCCs are also

Configuration	V_0 (Å ³ /atom)	ΔE_0 (meV/atom)	B_0 (GPa)	B'
NCC	16.5247	0.0000	78.548	4.906
SCC1	16.5253	-0.2162	78.543	4.871
SCC2	16.5257	-0.3164	78.332	4.980
SCC3	16.5252	-0.0388	78.568	4.883
SCC4	16.5258	-0.3498	78.277	5.011
AV (SCCs)	16.5255	-0.2303	78.430	4.936
SD (SCCs)	0.0003	0.1210	0.127	0.060

shown.

Table S 2: Equilibrium properties of YBCO (YBa₂Cu₃O₇) by EOS fitting using Birch-Morhaham EOS.

	V_0 (Å ³ /f.u.)	B_0 (GPa)	B'
Calc. (This work)	173.73	120.3	5.35
Expt.	173.43 ^a	115 ^b	

^a Measured data at 297 K by X-ray and neutron powder diffraction (24).

^b This value was believed as the best bulk modulus using high-pressure X-ray diffraction (32).

Table S 3: List of VASP POSCAR files for key structures used in the present work as attachments. The POSCAR files for LaH_{10} at various pressures were reported in the literature (8).

File name	Description
POSCAR_AL_NCC_2.6GPa	Structure file of Al NCC under pressure of 2.6 GPa
POSCAR_AL_SCC1_2.6GPa	Structure file of Al SCC1 under pressure of 2.6 GPa
POSCAR_AL_SCC1_2.6GPa	Structure file of Al SCC2 under pressure of 2.6 GPa
POSCAR_AL_SCC1_2.6GPa	Structure file of Al SCC3 under pressure of 2.6 GPa
POSCAR_AL_SCC1_2.6GPa	Structure file of Al SCC4 under pressure of 2.6 GPa
POSCAR_Nb3Sn_NCC_14.4GPa	Structure file of Nb ₃ Sn NCC under pressure of 14.4 GPa
POSCAR_Nb3Sn_SCC1_14.4GPa	Structure file of Nb ₃ Sn SCC1 under pressure of 14.4 GPa
POSCAR_Nb3Sn_SCC2_14.4GPa	Structure file of Nb ₃ Sn SCC2 under pressure of 14.4 GPa
POSCAR_Nb3Sn_SCC3_14.4GPa	Structure file of Nb ₃ Sn SCC3 under pressure of 14.4 GPa
POSCAR_YBCO_R2SCAN_0.1GPa	Structure file of YBCO under pressure of 0.1 GPa predicted
	by r ² SCAN.