COMMENTARY

Unifying guiding principles for designing optimized superconductors

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Cuprate high-temperature superconductors (HTS), discovered in 1986, are the only practical superconductors which can operate at liquid nitrogen temperature (77 K) in any moderate magnetic field. Liquid nitrogen is cheap and abundant and so is ideal. HTS has the capability to give clean energy across many application areas, for example, in motors, generators, power cables, levitation trains, fusion magnets, and medical imagery, and a huge effort has been put into the technological development over the last three decades, supported by intense theoretical investigations. An archetypal theory to model the copper oxides is the so-called Hubbard model. Such theories allow identification of key quantities that can provide markers to optimize the superconducting temperature (ideally, for room-temperature operations) and guide the chemical design of optimized materials. However, such endeavors are hampered by the many degrees of freedom, such as hole content, stoichiometry, covalency, and charge-transfer gap for the parent compound, and obtaining from the theory the key causal mechanisms for superconductivity is necessary to extract guiding principles (1, 2).

The Hubbard model remains, however, a stumbling block on which theorists have dedicated tremendous effort to break down a so-called many-body theory. The fermionic quantum many-body problem lies in the class of problems whose full solution is exponentially hard, which involves an exponential growth of computing resources as the number of electrons increases, hindering computational material design, and hampering both calculations and fundamental understanding. Quantum embedding approaches developed in the last three decades have offered a pathway to mitigate this inherent complexity, by using proxy local quantum theories for describing the strong electronic correlations. A typical example is the dynamical mean-field theory (DMFT) (3), which accounts for local correlation effects, and its extension, the cluster DMFT approach, that also provides superexchange and superconducting pairing across nearest-neighbor copper atoms (4). The latter numerical approaches involve sophisticated implementation of quantum Monte Carlo and remain demanding, requiring considerable computational resources. A body of work starting with ref. 5. has shown that the Hubbard model describes, indeed, many qualitative properties of the copper oxygen layers, but the precise energy range over which the description is valid and the quality of this description for different observables is still a subject of active research. This representation hinders the research of identifying atomistic parameters which could correlate with the presence of superconductivity: All the variables are effectively embedded in a single number, U/t, where U is the effective Coulomb repulsion and t is the hopping amplitude. Although the model captures the key ingredients, and, in particular, the localization/delocalization transition induced by the competition between the Coulomb repulsion term and the bandwidth, the correspondence between the model parameters U, t and the chemistry of the copper oxide compounds isn't transparent.

A key question is hence how to use a consistent mapping between the copper oxide layers onto relevant effective low-energy theories, and what are the corresponding parameters (transfer integrals, on-site potentials) in their relation to the materials of interest. This is paramount to guide the design of the next generation of HTS materials, building upon guidance from quantitative accurate theoretical predictions.

In PNAS, Kowalski et al. (1) explore the connection between covalency and the charge-transfer gap with superconducting pairing. They address this question by extending the Hubbard model to a multiband theory (6, 7), where the covalent bonding between copper and oxygen is captured in the theory.

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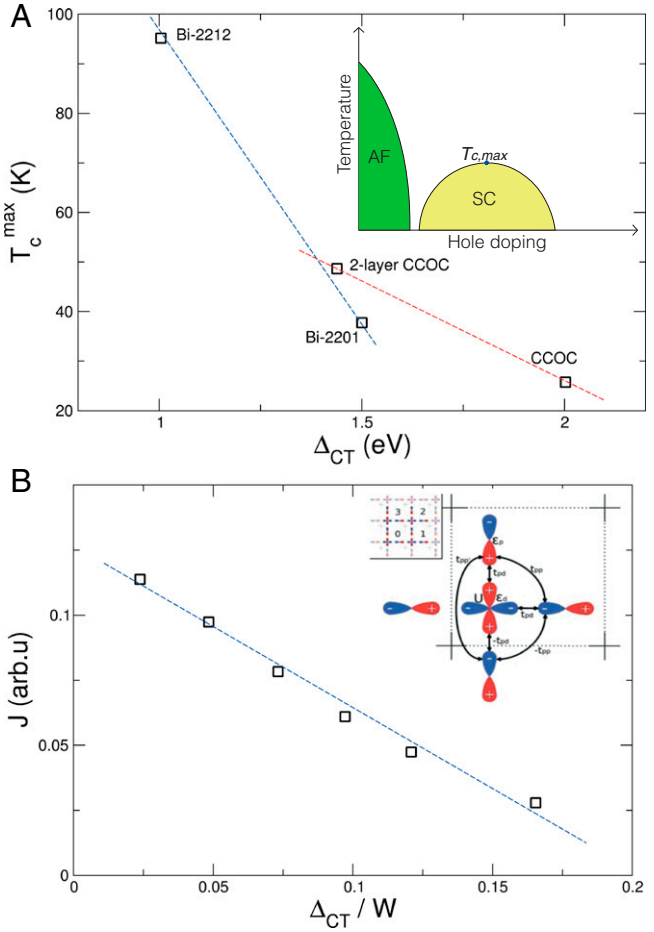

Fig. 1. (*A*) The experimental maximum superconducting temperature (T_c^{max}, see *Inset*) measured for $Ca_2CuO_2Cl_2$ (CCOC) and $Bi_2(Sr,La)_2CuO_{6+\delta}$ (Bi-2201) in monolayer and bilayer forms, as a function of the charge-transfer gap Δ_{CT} measured in the parent compound, and (*B*) the superexchange coupling *J* as a function of Δ_{CT} normalized by the bandwidth *W* by Kowalski et al. (1). Data from ref. 9. The pairing order parameter is known to correlate with the superexchange coupling (see ref. 9), so, in both instances, the maximum of the superconducting order parameters anticorrelates with the charge gap of the parent compound. The calculations solve a multiorbital theory with local repulsion *U* on copper atoms, hybridized with the in-plane oxygen orbitals (see *Inset*).

This opens possibilities for identifying a relation between superconductivity and chemical properties, in particular, the charge-transfer energy (an energy cost to displace an electron from a copper onto an oxygen that bridges two coppers) and the degree of covalency. This opens possibilities to establish missing links between theory and experiments. In particular, Kowalski et al. solve the three-band Hubbard model with cellular DMFT and show that this observation follows from the model.

As the parent compounds of the copper oxides are insulating, a landmark quantity is the charge gap. In the framework of the one-band Hubbard theory, the insulating properties are understood as the result of Mott physics associated with the increase of the electronic mass due to the strong Coulomb repulsion. This picture remains valid for the extended case of hybridized copper and oxygen hybrid molecular orbitals, but the role of electronic correlations isn't, in the latter case, only obtained by the amplitude of the Coulomb repulsion. In the latter, the strength of correlation is controlled by the Madelung charge-transfer energy between the *d* and *p* orbitals (8).

In this light, Kowalski et al. (1) report comparisons of charge and spin properties systematically for the three-band Hubbard model, inferring on the dependence of the superconducting order parameter with charge-transfer gap and superexchange coupling (see Fig. 1). In particular, the charge-transfer energy is a localized and an atomic-like quantity, which can be calculated by density functional theory in the normal state, and hence their work opens avenues for a direct comparison between theory and experiments. How superconductivity relates to the normal state has been a long-standing question, which can be addressed by first-principle calculations.

Recently, it has been shown, within the framework of numerical approaches of the Hubbard model, that there is an organizing principle: The superconducting order parameter is maximum for a Coulomb repulsion corresponding to the metal–insulator transition (10). At the transition, both localized and itinerant electrons coexist and provide the ideal glue for superconductivity. This has also been suggested in a recent work on the scaling of Tc with charge-transfer energy among cuprates (11).

Kowalski et al. (1) identify a paradigm in this light, the degree of covalency. Compounds with either ionic or covalent bonds have similar charge-transfer gaps, albeit they identify a direct correlation with the superconducting temperature. This is an important parameter that was not factored into earlier attempts to explain general trends of the superconducting temperatures across the family of materials.

For example, early theoretical work by Ohta et al. (12) found correlations between T_c and the Madelung potential of the apical oxygen, arguing that the apical potential controls the stability of the Zhang–Rice singlets. It was argued that the apical distance plays an important role in the electronic structure (13), principally via its effect on the apical and copper hybridization and the associated band structure.

However, none of the aforementioned work could explain the trend of the maximum superconducting temperature (typically obtained in optimally doped compounds) with the charge gap of the parent compound. Experiments have indeed reported a striking anticorrelation relation between the two latter quantities (9). Strikingly, the work of Kowalski et al. (1) provides a similar trend between the superconducting order parameter of the optimally doped system, a known proxy for estimating the superconducting temperature, and the charge-transfer gap.

In their work (1), Kowalski et al. identify the relevant energy scales which control, ultimately, the critical temperature, and add a so far missing link to this picture: The ionic compounds tend to have lesser effective superexchange coupling, which is detrimental for pairing. The suppression of the superconducting order parameter with the charge-transfer gap also suggests that the superexchange is at play, since the charge-transfer gap in a charge-transfer system plays the role of a Mott gap in the single-band Hubbard model, a marker to quantify the strength of correlations for the Mott transition. To this end, they calculated a complex mathematical object, the so-called two-particle electronic propagator, a tour de force in the context of such a complex many-body theory.

Kowalski et al.'s (1) work sheds light on the classification of the parent compounds of copper oxide superconductors and their associated low-energy theoretical descriptions. This will motivate future work to obtain a clearer picture of the relation between the maximum of the superconducting order parameter and the structural parameters associated with the chemistry of the parent materials, a vital task for screening promising high-Tc materials.

They also extract the essential energy scale, the charge-transfer gap, which relates to the optimally doped superconducting order parameter on a broad range of parameters. Strikingly, this quantity is obtained in the parent compound, whereas the optimally doped properties are observed after complex chemical substitutions across the copper oxides' phase diagram.

The latter is rationalized by the degree of covalency that relates to superexchange and the formation of short-range Cooper pairs in HTS. Kowalski et al.'s (1) work sheds light and rationalizes recent experimental data (9), and accounts for the trend in superconducting temperatures across the cuprate families, which opens a direction for designing in the future materials with optimal properties.

1 N. Kowalski, S. S. Dash, P. Sémon, D. Sénéchal, A.-M. Tremblay, Oxygen hole content, charge-transfer gap, covalency, and cuprate superconductivity. *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2106476118 (2021).
2 C. Weber, What controls the critical temperature of high temperature copper oxide superconductors: Insights from scanneling tunnelling microscopy. *Sci. Bull. (Beijing)* **62**, 102–104 (2017).
3 A. Georges, G. Kotliar, W. Krauth, Superconductivity in the two-band Hubbard model in infinite dimensions. *Z. Phys. B Condens. Matter* **92**, 313–321 (1993).
4 K. Haule, G. Kotliar, Strongly correlated superconductivity: A plaquette dynamical mean-field theory study. *Phys. Rev. B Condens. Matter Mater. Phys.* **76**, 104509 (2007).
5 F. C. Zhang, T. M. Rice, Effective Hamiltonian for the superconducting Cu oxides. *Phys. Rev. B Condens. Matter* **37**, 3759–3761 (1988).
6 V. J. Emery, Theory of high-Tc superconductivity in oxides. *Phys. Rev. Lett.* **58**, 2794–2797 (1987).
7 C. M. Varma, S. Schmitt-Rink, E. Abrahams, Charge transfer excitations and superconductivity in "ionic" metals. *Solid State Commun.* **62**, 681–685 (1987).
8 J. Zaanen, G. A. Sawatzky, J. W. Allen, Band gaps and electronic structure of transition-metal compounds. *Phys. Rev. Lett.* **55**, 418–421 (1985).
9 W. Ruan *et al.*, Relationship between the parent charge transfer gap and maximum transition temperature in cuprates. *Sci. Bull. (Beijing)* **61**, 1826–1832 (2016).
10 L. Fratino, P. Sémon, G. Sordi, A. M. S. Tremblay, An organizing principle for two-dimensional strongly correlated superconductivity. *Sci. Rep.* **6**, 22715 (2016).
11 C. Weber, C. Yee, K. Haule, G. Kotliar, Scaling of the transition temperature of hole-doped cuprate superconductors with the charge-transfer energy *EPL* **100**, 37001 (2012).
12 Y. Ohta, T. Tohyama, S. Maekawa, Apex oxygen and critical temperature in copper oxide superconductors: Universal correlation with the stability of local singlets. *Phys. Rev. B* **43**, 2968 (1991).
13 E. Pavarini, I. Dasgupta, T. Saha-Dasgupta, O. Jepsen, O. K. Andersen, Band-structure trend in hole-doped cuprates and correlation with T(c max). *Phys. Rev. Lett.* **87**, 047003 (2001).