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A brief pictorial description of the large-bipolaron-liquid model of cuprate superconductivity

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ABSTRACT

Media containing exceptionally displaceable ions supports self-trapped bipolarons that can move coherently since they extend over multiple sites. Such strong-coupling "large" bipolarons are distinguished from conventional charge carriers by their huge effective masses, unusual phonon scattering, distinctive mobilities and frequency-dependent conductivities. Phonon-mediated mutual attractions between such self-trapping large bipolarons can foster their condensation into charged Bose liquids that can further condense into a superconducting ground state. A chemical model for hole-doped cuprates has self-trapped electronic $(O_4)^{2-}$ units eliminating spins on surrounding Cu^{2+} cations while producing a *d*-symmetry superconducting ground state.

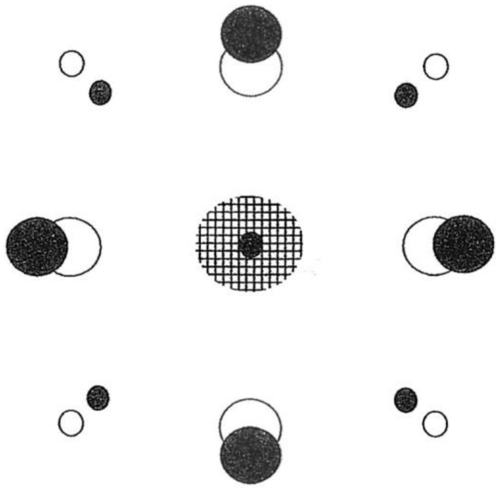


Fig. 1.1 An excess electron (hatched area) held on a cation shifts the equilibrium positions of the surrounding anions (filled large circles) and cations (filled small circles) from their carrier-free positions (open large and small circles). These shifts of ions' equilibrium positions produce a potential well for that carrier.

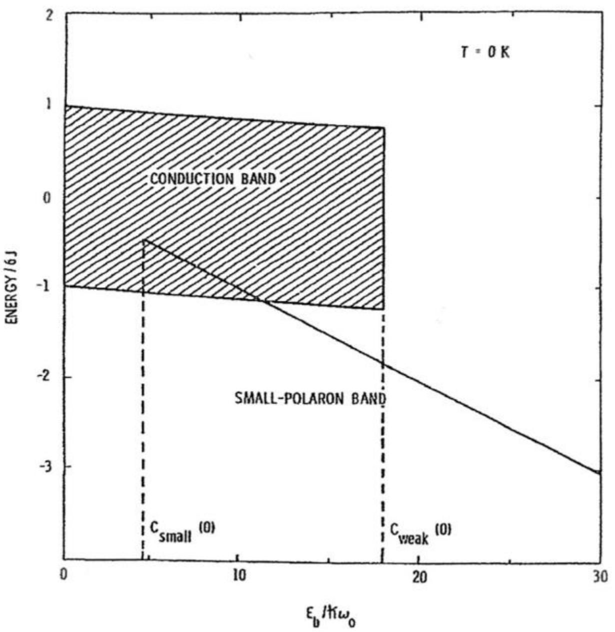
D. Emin, *Polarons* (Cambridge, 2013) Fig. 1.1

Fig. 1 Self-trapping of an electronic carrier extends condensed matters' adiabatic approach: electrons readily adjust to relatively slow atomic motions. A self-trapped electronic charge carrier is bound with an energy exceeding a characteristic phonon energy in the potential well generated by the surrounding atoms' displaced equilibrium positions that its very presence stabilizes [L. D. Landau, Phys. Z. Sowjetunion 3, 644 (1933)].

Short-range (e.g., deformation-potential) electron-lattice interactions result from an electronic carrier's energy depending strongly on the separations between the atoms which it contacts. Long-range electron-lattice interactions result from an electronic carrier's Coulomb energy depending on its distances from ionic (polar) materials' remote displaceable ions.

Self-trapping occurs in many types of condensed matter. Nonetheless, since self-trapping was first considered in *polar* solids, the composite particle comprising a self-trapped electronic carrier and the associated displaced atomic equilibrium positions was dubbed a strong-coupling *polaron* or self-trapping *polaron.* By contrast, a weak-coupling polaron's electronic carrier is not self-trapped; it just adjusts to atoms' harmonic vibrations thereby altering their frequencies.

A *small* polaron's self-trapped electronic carrier collapses to a single structural unit, rendering its inter-site motion incoherent (e.g., by phonon-assisted hopping). A *large* polaron's self-trapped electronic carrier extends over multiple sites rendering its motion coherent. This very massive and slow-moving quasiparticle has qualitatively different properties than those of conventional electronic carriers.



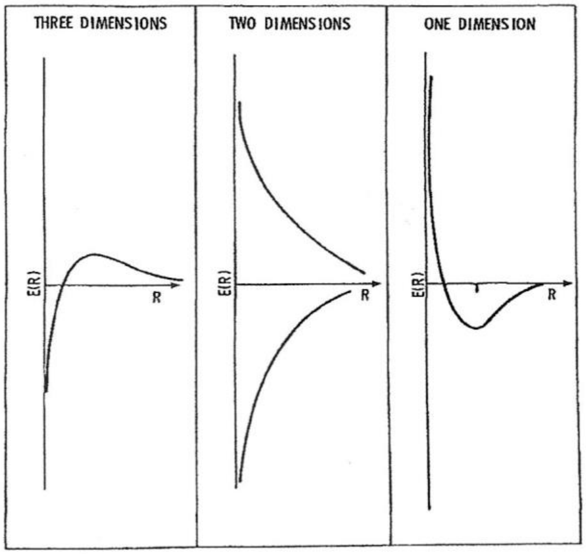
The one-electron energy spectrum is plotted as a function of the electron–lattice coupling strength, defined as $E_b/\hbar\omega_0$, for $6J/\hbar\omega_0=10$ at $T=0$ K. The energy of the coupled system minus the zero-point vibrational energy, $n\hbar\omega_0/2$, is measured in units of the rigid-lattice band half-width, $6J$.

D. Emin, *On the existence of free and self-trapped carriers in insulators: An abrupt temperature-dependent conductivity transition*, Adv. Phys. 22, 57-116 (1973) Fig. 4

Fig. 2 An electronic carrier's short-range interactions with displaceable atoms in a three-dimensional molecular crystal only produce a small-polaron's collapsed (single-site) self-trapped state [D. Emin, Phys. Rev. Lett. 28, 604-607 (1972)]. Beyond the adiabatic limit [$C_{small}(T) \rightarrow 0$ and $C_{weak}(T) \rightarrow \infty$], small polarons are only possible (dynamically stable) for sufficiently strong electron-lattice interactions, > $C_{small}(T)$. Non-polarons are only possible (dynamically stable) for sufficiently weak electron-lattice interactions, < $C_{weak}(T)$.

Raising the temperature increases $C_{weak}(T)$ as increasing atoms' vibratory momenta reduces transiting electronic carrier's ability to displace them. This effect enables abrupt conductivity transitions in which thermally induced high-mobility conduction-band transport overwhelms very-low-mobility small-polaron transport.

Imposing even modest disorder decreases $C_{weak}(T)$ by eliminating sites required for non-polaronic conduction [D. Emin and M.-N. Bussac, Phys. Rev. B, 14290-14300 (1994)]. For example, the resulting small polarons are indicated by chalcogenide glasses' distinctive electronic transport [D. Emin, C. H. Seager and R. K. Quinn, Phys. Rev. Lett. 28, 813-818 (1972)].



The energy of the system comprising an electron and deformable continuum is plotted against the scaling factor R, which is related to the size of the polaron. A finite-radius polaron in this system is energetically stable only when the system is restricted to one dimension.

D. Emin, *On the existence of free and self-trapped carriers in insulators: An abrupt temperature-dependent conductivity transition,* Adv. Phys. 22, 57-116 (1973) Fig. 8

Fig. 3 The adiabatic limit has atoms' infinite masses suppressing their vibrations. In this limit, consistent with the results displayed in the prior figure, an electronic carrier self-trapped via a short-range interaction in a multi-dimensional deformable medium can only collapse into a small polaron. As illustrated above [D. Emin, Adv. Phys. 22, 57-116 (1973)], Holstein's finding that a short-range interaction yields a large-polaron with its finite-radius self-trapped state [T. Holstein, Ann. Phys. (N.Y.) 8, 325-342 (1959)] is an artifact of its model's one-dimensionality. Moreover, this one-dimensional behavior requires extreme electronic anisotropy [D. Emin, Phys. Rev. B 33, 3973-3975 (1986); H.-B. Schüttler and T. Holstein, Ann. Phys. (N.Y.) 166, 93-163 (1986) Sec. 7].

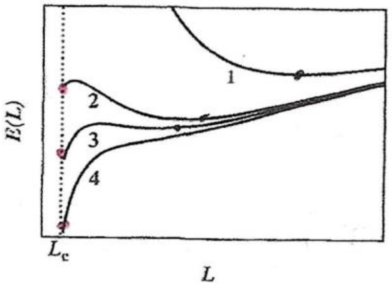


Fig. 4.4 The large-polaron minimum (curve 1) shrinks and falls in energy as the short-range interaction increases. As the short-range interaction strengthens (curve 2) a meta-stable small-polaron minimum appears at L_c. The small polaron is stabilized as the interaction is increased further (curve 3). Ultimately (curve 4) the large-polaron minimum disappears.

D. Emin, *Polarons* (Cambridge, 2013) Fig. 4.4

Fig. 4 As illustrated above, by itself, in the adiabatic limit an electronic carrier's long-range interactions with distant displaceable ions in a three-dimensional ionic continuum produces a large polaron's finite-radius self-trapped state [S. I. Pekar, Untersuchungen über die electronentheorie der kristalle (Academic-Verlag, Berlin 1954)]. Acting in tandem, three-dimensional long-range and multi-dimensional short-range components of electron-lattice interactions can produce coexisting self-trapped large-polaron and small-polaron states, one energetically stable, the other energetically metastable [D. Emin and T. Holstein, Phys. Rev. Lett. 36, 323-326 (1976)]. Only a small polaron survives a sufficiently strong short-range component.

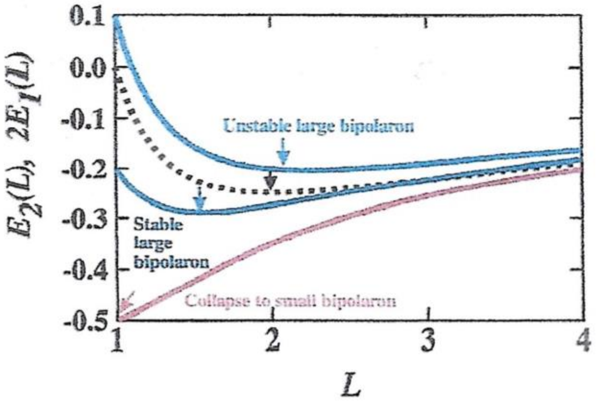


Figure 1. (colour online) Solid curves plot a bipolaron's energy functional $E_2(L)$ for three values of the in-plane electron–phonon interaction V_p against the scaling length L. The dashed curve plots the energy functional for two separate polarons $2E_1(L)$ with $V_p = 0$ against the scaling length L. The adiabatic energies are at these curves' minima (indicated with arrows). Comparing the uppermost solid curve (for $V_p = 0$) with the dashed curve shows that the large bipolaron is unstable with respect to two separate large polarons. Increasing V_p can stabilise large-bipolaron formation. The red curve shows the bipolaron collapsing into a small bipolaron if V_p is too large, c.f. Equation (4).

D. Emin, *Dynamic d-symmetry Bose condensate of a planar large-bipolaron-liquid in cuprate superconductor*s, Phil. Mag. 97, 2931-2945 (2017) Fig. 1

Fig. 5 A simple bipolaron forms when two electronic carriers self-trap as a singlet pair occupying a common orbital. Here large bipolaron and separated large polarons are treated as strongly coupled $(\alpha \gg 1)$within the standard Fröhlich model. Then ions' displaceabilities are proportional to the difference between the reciprocals of a material's high-frequency and static dielectric constants. With only the long-range component of the electron-lattice interaction this simple large-bipolaron is energetically unstable with respect to separating into two large olarons. The addition of the short-range component of the electron-lattice interaction can stabilize this simple large bipolaron. However, too strong a short-range component will drive a large-bipolaron's collapse into a small-bipolaron. For a stable planar large bipolaron embedded within a three-dimensional ionic medium, the ratio of twice a single carrier's short-range interaction strength to an electronic carrier's bandwidth, $2V_S/T$, must satisfy $\frac{[4(\varepsilon_0/2\varepsilon_\infty)-3]}{[2(\varepsilon_0/2\varepsilon_\infty)^2-1]} < \frac{2V_S}{T} < 1$ [D. Emin, *Polarons*, (Cambridge 2013) Eq. 7.5]. Thus, stable large-bipolarons require unusually large ratios of a material's static to high-frequency dielectric constants: $\varepsilon_0/\varepsilon_\infty \gg 2,$ indicating exceptionally displaceable ions (e.g. many perovskites) [D. Emin, Phys. Rev. Lett. 62, 1544-1547 (1989); D. Emin and M. S. Hillery, Phys. Rev. B 39, 6575-6573 (1989)].

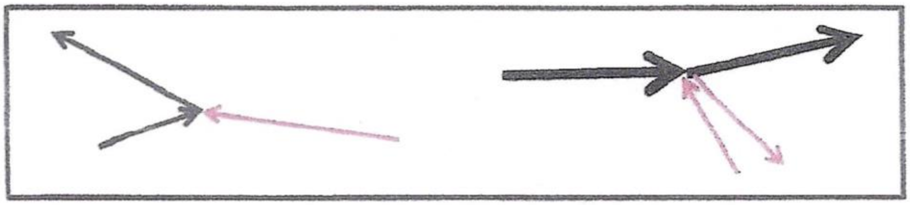


Figure 5. (colour online) The strong scattering of a light fast-moving conventional electronic carrier produced by the absorption of a relatively large-momentum acoustic phonon (red arrow) depicted on the left is qualitative different from the very weak scattering of a heavy slow-moving large bipolaron generated by its 'reflection' of a relatively small-momentum long-wavelength acoustic phonon depicted on the right.

D. Emin, *Dynamic d-symmetry Bose condensate of a planar large-bipolaron-liquid in cuprate superconductors,* Phil. Mag. 97, 2931-2945 (2017) Fig. 5

Fig. 6 A large (bi)polaron moves very slowly with a huge effective mass since its motion requires significant atomic shifts. Moreover, vibrations of the atoms whose displaced equilibrium positions generate a large-(bi)polaron are softened as its self-trapped carriers adjust to them. Due to a large (bi)polaron's huge effective mass, it is only very weakly scattered as its softened phonons "reflect" dispersive ambient phonons with comparable wavelengths. This very weak scattering compensates for a large-(bi)polaron's huge effective mass to produce the room-temperature mobility: $\mu \sim qR^2\nu/kT$, about 1 cm^2/V-s at 300 K. Here q, R and ν indicate a bipolaron's charge, its self-trapped carriers' radius and a representative phonon frequency [H.-B. Schüttler and T. Holstein, Ann. Phys. (N.Y.) 166, 93-163 (1986)]. This mobility is usually well below the minimum for a conventional electronic carrier of mass m: $q\hbar/mkT$, about 45 cm^2/V-s at 300 K with m being the free-electron mass. [D. Emin, *Polarons* (Cambridge, 2013) Eq. (10.1)].

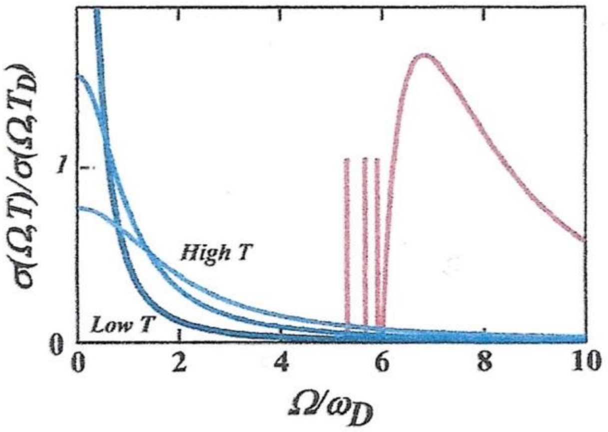


Figure 6. (colour online) The frequency-dependent conductivity of a large-bipolaron liquid $\sigma(\Omega, T)$ has two distinct components. At applied frequencies Ω primarily below the Debye frequency ω_D, large-bipolarons' collective motion generates temperature-dependent Drude-like contributions (depicted by blue curves). At frequencies well above ω_D, optical liberation of large-bipolarons' self-trapped electronic carriers produces an asymmetric band (plotted in red). At somewhat lower frequencies, self-trapped carriers can be excited to states within their self-trapping potential wells (illustrated with several vertical red lines). The 'gap' between the low- and high-frequency contributions opens as the temperature is lowered.

D. Emin, *Dynamic d-symmetry Bose condensate of a planar large-bipolaron-liquid in cuprate superconductors*, Phil. Mag. 97, 2931-2945 (2017) Fig. 6

Fig. 7 A large-(bi)polaron's very weak scattering drives the Drude fall-off of its frequency-dependent conductivity to extremely low frequencies that fall with decreasing temperature. These frequencies are well below the almost temperature-independent distinctively asymmetric band associated with photo-liberation of a large bipolaron's self-trapped electronic carriers [D. Emin, Phys. Rev. B 48, 13691-13702 (1993)]. The Drude fall-off is also presumably below any potential absorptions associated with exciting a large-bipolaron's self-trapped carriers to levels within their self-trapping potential well. The temperature-dependent separation between self-trapping large (bi)polarons' very low frequency temperature-dependent Drude absorption and their intrinsic absorption explains the "pseudo gap" observed in cuprates [D. Emin, Phil. Mag. 97, 2931-2945 (2017)].

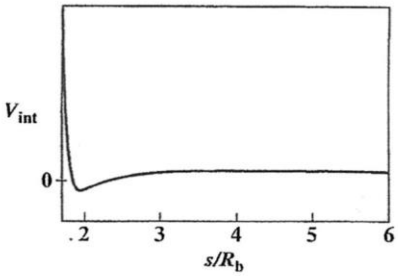


Fig. 14.1 When the static dielectric constant is sufficiently large the interaction potential V_{int} comprising the three components described in Section 14.1 develops a minimum at a separation between large bipolarons s which is near twice the bipolaron radius R_b.

D. Emin, *Polarons* (Cambridge, 2013) Fig. 14.1

Fig. 8 Phonon-mediated attractions between large bipolarons occur because softening of their zero-point phonon frequencies is enhanced for phonon-wavelengths exceeding their separations. [D. Emin, Rev. Lett. 72, 1052-1055 (1994); Phys. Rev. B 49, 9157-9167 (1994)]. These intermediate range phonon-mediated attractions between large bipolarons can overwhelm their mutual long-range Coulomb repulsions if suppressed by a material’s large static dielectric constant. Meanwhile, large-bipolarons' short range hard-core repulsions prevent their merging into even grander polarons. Then intermediate-range attractions can drive large bipolarons condensing into a charged Bose liquid.

The phonon-mediated attraction between large-bipolarons which drives liquid formation is akin to that between weak-coupled carriers which drives their BCS pairing. Both effects vanish when atomic vibrations are suppressed.

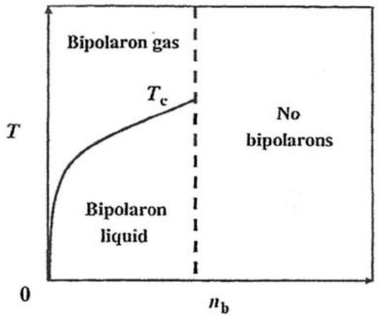


Fig. 14.2 Phonon-mediated attractions between large bipolarons enable them to condense from a gas of nearly independent quasi-particles into a liquid phase. Condensation begins when the temperature T is lowered below the condensation temperature T_c. The condensation temperature rises with the large-bipolaron density n_b. However, large bipolarons cannot form beyond a maximum limiting density depicted by the vertical dashed limit.

D. Emin, *Polarons* (Cambridge, 2013) Fig. 14.2

Fig. 9 The liquid comprising mutually attractive large bipolarons presumably undergoes a Bose condensation into a superconducting state unless its ground state solidifies. The elementary excitations of a charged liquid are its plasma oscillations. The superconducting transition temperature of a large-bipolaron liquid roughly corresponds to its plasma energy [D. Emin, Phil. Mag, 95, 918-934 (2015)]. Large-bipolarons' modest densities, huge effective masses, and host-materials' very large static dielectric constants generate transition temperatures of about 100 K in cuprates. Solidification occurs when large bipolarons order commensurate with the host material's underlying lattice. For cuprates with square basal planes, planar superconductivity is lost at pre-paired carrier densities of 2/(5x5), 2/(4x4) and 2/(3x3). Strikingly, superconductivity of simple cuprates is observed to vanish at a dopant density of 1/8 = 12.5%, within their broad superconducting regime, about 6 – 22%.

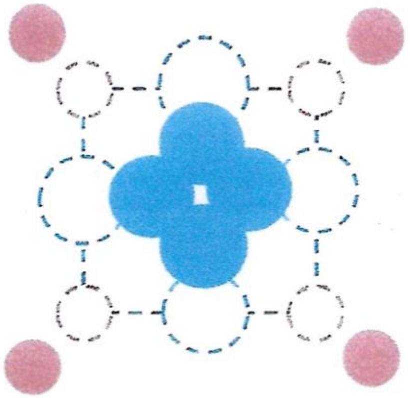


FIG. 1. A superoxygen dianion forms as a pair of holes added to oxygen anions (blue circles) of a CuO_2 unit induces them to move inward as copper cations (red circles) move outward. Concomitant transfers of electrons to these copper cations eliminate their spins.

D. Emin, *Large-bipolaron-liquids in cuprate superconductors*, J. Chem. Phys. 160, 210901 (2024) Fig. 1

Fig. 10 For doped-La_2CuO_4 quasi-planar large-bipolarons are centered on less than 10% of their CuO_2 units. A large-bipolaron's singlet pair of self-trapped holes primarily occupy the *super-oxygen* O_4 comprising four inwardly displaced oxygens circumscribed by four outwardly displaced copper ions of a CuO_2 unit. The electron affinity of each of these oxygen atoms is only 1 (that of an isolated oxygen atom), thereby releasing one of its electrons to surrounding copper atoms: 2 holes + $4(O^{2-}) + 4(Cu^{2+}) \rightarrow (O_4)^{2-} + 4(Cu^{+1})$. The singlet electron pair of the $(O_4)^{2-}$ super oxide occupies a molecular orbital involving its four out-of-plane oxygen orbitals. Each such bipolaron also replaces four spin-½ Cu^{2+} ions with four spinless Cu^{1+} ions [D. Emin, J. Chem. Phys. 160, 210901 (2024)].

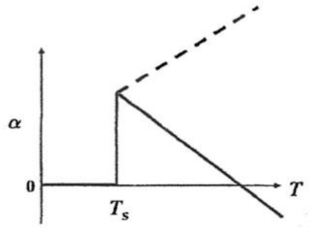


Fig. 14.6 The Seebeck coefficient α of a superconductor vanishes when the temperature T is lowered below the superconducting transition temperature T_s. When $T > T_s$ the Seebeck coefficient of a conventional *p*-type superconductor rises with increasing temperature (dashed line). If, however, large-bipolaron formation eliminates local magnetic moments, the Seebeck coefficient of a *p*-type cuprate superconductor may fall and even change sign as the temperature is raised (solid line).

D. Emin, *Polarons* (Cambridge, 2013) Fig. 14.6

Fig. 11 The Seebeck coefficient is the entropy transported with a charge carrier divided by its charge. For hole-like large bipolarons in simple cuprates the standard (carrier-induced change of the entropy-of-mixing) contribution is positive. By comparison, the large-bipolaron induced replacement of four spin-½ Cu^{2+} ions by four spinless Cu^{1+} ions generates a negative contribution. The magnitudes of both contributions rise with increasing temperature. In the high-temperature paramagnetic limit, these contributions respectively become $(k/2e)\ \ln[(1-c)/c]$ and $-\ (4k/2e)\ \ln(2)$: [D. Emin, J. Appl. Phys. 119, 045101 (2016)]. Here *k, e* and *c* denote the Boltzmann constant, the magnitude of an electron's charge, and the large-bipolaron concentration. Therefore, as schematically illustrated, the Seebeck coefficients of cuprate superconductors differ in magnitudes, temperature dependencies and even in signs from those of a superconducting metal's normal state.

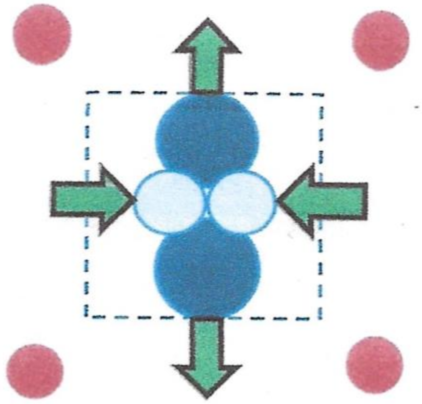


FIG. 2. Arrows depict the relative movements of oxygen-anions for the lowest-frequency and largest-zero-point-amplitude normal radial vibrational mode. The $(O_4)^{2-}$ molecular orbital's two added electrons adiabatically transfer from inward moving oxygens (lightened blue circles) to outward moving oxygens (darkened blue circles) that are closer to the surrounding copper cations.

D. Emin, *Large-bipolaron-liquids in cuprate superconductors*, J. Chem. Phys. 160, 210901 (2024) Fig. 2

Fig. 12 Oxygen atoms of $(O_4)^{2-}$ super-oxygen dianions radially vibrate against surrounding Cu^{+1} cation cages. Couplings between neighboring oxygens separate the four resulting optic vibrations into one with *s*-symmetry, two with *p*-symmetry and one with *d*-symmetry. The zero-point vibration with *d*-symmetry has the lowest energy and the largest amplitude [D. Emin, Phil. Mag. 97, 2931-2945 (2017)]. As illustrated, the self-trapped singlet pair adiabatically adjusts to these vibrations. The uniformity of the superconducting large-bipolaron liquid's collective ground state suggests that all of its interacting super-oxygen dianions share a common *d*-symmetry alignment.