Exciton self-trapping processes

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Abstract: Small-radius Frenkel excitons coupled with phonons can have diverse configurational structures depending on the symmetry of the electronic states involved and that of the associated modes of the inter-ionic/molecular vibrations. It is considered here that the symmetric excitons arise from the coupling with symmetry-retaining vibrational modes and vibronic excitons from the coupling to symmetry-breaking modes. Three examples are discussed: (i) formation of the barriers of exciton self trapping, as it occurs in the dimer formation at semiconductor surfaces, (ii) parity breaking that occurs at a centrosymmetric site and leads to an inversion electric dipole which enhances the polarizability and binding energy for pairing vibronic excitons, and (iii) a Bose condensation model of quasi-2D excitons applicable to the layered materials.

INTRODUCTION

Excitons in crystalline solids have been studied extensively (1-3). An exciton can couple to the phonon field resulting in a lattice distortion around itself. The form of lattice distortion depends on the symmetry of the associated lattice vibration. The motion of a phonon-coupled exciton in a deformable lattice is hindered by its accompanying distortion. An exciton accompanied by a lattice distortion is defined here as an excitonic polaron. Now the character of the lattice distortion depends on the magnitude and spatial range of the carrier-phonon coupling, and dimensionality of exciton motion. For example, if the exciton couples strongly with the atomic displacements in its neighbourhood, a short-range distortion (shrunk distortion) arises leading to a small excitonic polaron. In three dimensions (3-D) the distortion is always shrunk (short range), but in one dimension (1-D) it is of a long range (spatially extended) at weak coupling and gradually shrinks as the coupling increases. The two-dimensional (2-D) self-trapping is an interplay of 1-D and 3-D features (4). Excitonic polaron mobile at weak coupling may become immobilized or self-trapped at strong coupling. There exists a barrier between free and self-trapped state as first pointed out by Rashba (5).

In this paper, we have studied the effect of symmetry of the associated lattice vibrations on the behaviour of small excitonic polarons (6). Non-degenerate electronic states can only couple to symmetry-retaining vibrational modes and create symmetric distortions. However, degenerate or nearly-degenerate states coupled strongly with the symmetry breaking modes, may lead to vibronic excitons (7). Off-centered vibronic excitons may be formed if the original site-symmetry incorporates the spatial inversion.

SMALL EXCITONIC POLARONS

The Hamiltonian of a Frenkel exciton coupled to a lattice can be written as (2,6):

$$H = \sum_{lts} E_{lt}^+(s) B_{lt}^+(s) B_{lt}(s) + \sum_{(lm)tt's} \mathcal{J}_{lm}^{tt'}(s) B_{lt}^+(s) B_{mt'}(s) +$$
$$+ \sum_{ltt's} G_{ltt'}(s) Q_{ltt'} B_{lt}^+(s) B_{lt'}(s) + \frac{1}{2} \sum_{ltt'} \left(\frac{P_{ltt'}^2}{M_{ltt'}} + K_{ltt'} Q_{ltt'}^2 \right) \quad , \tag{1}$$

where $E_{lt}(s)$ and $B^+_{lt}(s)$ are the energy and creation operator of an exciton, respectively, with spin s in band t and localized at site l. $\mathcal{J}^{tt'}_{lm}(s)$ is the excitation transfer matrix element between sites l and m, and $P_{ltt'}$, $M_{ltt'}$ and $K_{ltt'}$ are the momentum, reduced mass and force constant of an interatomic mode of coordinate $Q_{ltt'}$, respectively, and $G_{ltt'}(s)$ is the corresponding coupling constant. As the Hamiltonian must be invariant with respect to the site point-group, the symmetry of the electronic levels and that of the coupled vibration is interdependent. For instance, the vibration will conserve the original site symmetry if the electronic levels are nondegenerate, but the symmetry will be destroyed if these levels are degenerate or nearly-degenerate. Symmetry-retaining polarons have been introduced by Holstein (8) a long time ago, while symmetry-breaking ones, such as Jahn-Teller and Pseudo-Jahn-Teller polarons (7), have drawn attention only more recently.

Writing the eigenstate of an excitonic polaron in a band t as a superposition of one-exciton states:

$$|t,s\rangle = \sum_l C_{lt}(s) B_{lt}^+(s) |0\rangle \quad , \tag{2}$$

we solve the Schroedinger's equation using the Hamiltonian of Eq.(1) without the kinetic energy operator of lattice vibrations (adiabatic). Thus we get a secular equation as:

$$\left[E_{lt}(s) + \frac{1}{2} \sum_{t't''} K_{lt't''} Q_{lt't''}^2 - E_{AD}(Q_{lt}) \right] C_{lt}(s) +$$
$$+ \sum_{t'} \left[G_{ltt'}(s) Q_{ltt'} + G_{lt't}(s) Q_{lt't} \right] C_{lt'}(s) + \sum_{(lm)} \mathcal{J}^{tt'}_{(lm)}(s) C_{mt}(s) = 0 \tag{3}$$

where $E_{AD}(t,s)$ is the adiabatic energy eigenvalue.

Symmetric Excitonic Polarons

We consider a two-site case, l and m, taking $m = l$-1 an only one energy band t in Eq.(3) to obtain a quadratic equation. Usually E_l, K_l and G_l are independent of the site l and $\mathcal{J}^{tt}_{l,l-1} = \mathcal{J}^{tt}_{l-1,l} = \mathcal{J}_l$ for nearest neighbors. For a symmetric mode, taking $Q_{ltt} = -Q_{l-1,tt} = Q_l$ we get:

$$E_{AD\pm}(Q_l) = E_l + \frac{1}{2} K_l Q_l^2 \pm \sqrt{G_l^2 Q_l^2 + \mathcal{J}_l^2} \quad , \tag{4}$$

where the band index t is dropped for simplification and $E_{AD\text{-}}(Q_l)$ thus obtained is a double-well potential for $|\mathcal{J}_l| < G_l^2/K_l$ centered symmetrically at $Q_l = 0$ with two side minima at $Q_{0\pm}$ given by:

$$Q_{0\pm} = \pm \frac{\sqrt{G^4 - K^2 \mathcal{J}^2}}{GK} \quad , \tag{5}$$

where we have assumed $G_l = G$, $K_l = K$ and $\mathcal{J}_l = \mathcal{J}$. The configurational distortions at $+Q_0$ and $-Q_0$ relate to the two sites at l and l-1, respectively. $E_{AD\text{-}}(Q)$ has a maximum at $Q = 0$ which forms a real barrier due to $\mathcal{J}$, and the exciton bandwidth, $2\mathcal{J}$, splits $E_{AD+}(Q)$ and $E_{AD\text{-}}(Q)$ at the symmetric point. The exciton-phonon coupling lowers the exciton energy below the peak of $E_{AD\text{-}}(Q)$ to form an excitonic polaron band.

Having solved the adiabatic problem, we consider $E_{AD\text{-}}(Q)$ as the potential in the Hamiltonian for a two site vibronic problem as:

$$H_{\text{vib}} = \frac{P^2}{2M} + E_{AD\text{-}}(Q) \quad , \tag{6}$$

where M is the reduced mass of a two site oscillator ($M^{-1} = M_l^{-1} + M_{l-1}^{-1}$). We solve the Schroedinger's equation by a linear combination of ground-state harmonic-oscillator wave- functions centered at the two wells. We thus obtain the fullwidth, $\delta\varepsilon_{vib}$, of the excitonic polaron band as:

$$\delta\varepsilon_{vib} = \mathcal{J}\left(1 - \frac{\mathcal{J}}{2E_{JT}}\right)\operatorname{cosech}\left\{\frac{2E_{JT}}{\hbar\omega}\left[1 - \left(\frac{\mathcal{J}}{2E_{JT}}\right)^2\right]\right\} \quad , \tag{7}$$

centered at E_P given by:

$$E_P = \frac{1}{2}\hbar\omega + E_l - E_{JT} - \frac{\mathcal{J}}{1-S^2}\left[(1+S^2)\frac{\mathcal{J}}{4E_{JT}} - S^2\right] \quad . \tag{8}$$

The binding energy of an excitonic polaron can be defined as $E_B = -E_P$. $S = \exp\{-(2E_{JT}/\hbar\omega)[1-(\mathcal{J}/2E_{JT})^2]\}$ is the overlap integral, and E_{JT} is defined as $E_{JT} = G^2/2K$, which is equivalent to the Jahn-Teller's energy for a degenerate case. Q_0 is real for $|\mathcal{J}| < 2E_{JT}$, the condition for forming a small excitonic polaron of radius proportional to E_B^{-1} (E_B in cm^{-1}).

Jahn-Teller (JT) Excitonic Polarons

We next consider a doubly-degenerate conduction band arising from two local levels (t and t'). We set the energy $E_{lt} = E_{lt'}$ ($= 0$) and assume the band-off-diagonal coupling to an interband-mixing mode independent of the site, as $Q_{ltt'} = Q_l = Q$. Using the two sites approximation again, we define a composite mode Q_l as $Q_l = Q\cos(\beta)$, $Q_{l-1} = Q\sin(\beta)$, which gives a symmetry-breaking component at $\beta = \pi/4$ leading to $Q_l = Q_{l-1} = Q/\sqrt{2}$. The corresponding APES is obtained as:

$$E_{AD\pm}(Q) = \frac{1}{2}\left[KQ^2 \pm \sqrt{4G^2Q^2 + 2(\mathcal{J}_t^2 + \mathcal{J}_{t'}^2) \pm 2|\mathcal{J}_t - \mathcal{J}_{t'}|\sqrt{4G^2Q^2 + (\mathcal{J}_t + \mathcal{J}_{t'})^2}}\right] \quad . \tag{9}$$

$E_{AD+}(Q)$ and $E_{AD-}(Q)$ split adiabatically at $Q = 0$ by $E_{AD+}(0) - E_{AD-}(0) = |\mathcal{J}_t| + |\mathcal{J}_{t'}|$, which is the effective free-exciton bandwidth. The JT excitonic polaron lowers the site symmetry without violating the parity conservation and induces a configurational distortion away from the symmetric site at $Q = 0$. The excitonic polaron hops between neighbouring sites inciting a local lattice distortion, while its energy falls down into a narrow excitonic polaron band.

Pseudo-Jahn-Teller (PJT) Excitonic Polarons

Here we consider a conduction band originating from two nearly- degenerate local levels, due to the inter-site coupling. We assume t and t' to be of opposite parities and set $E_{lt} = E_{l-1t} = -E_{lt'} = -E_{l-1t'} = -E_{tt'}/2$. Also, by setting $Q_l = Q_{l-1} = Q$, $K_l = K_{l-1} = K$ and $G_l = G_{l-1} = G/2$, and assuming $\mathcal{J}_t = \mathcal{J}_{t'} = \mathcal{J}$ we get:

$$E_{AD\pm}(Q) = \frac{1}{2}\left[KQ^2 \pm \left(\sqrt{4G^2Q^2 + E_{tt'}^2} \pm 2\mathcal{J}\right)\right] \quad . \tag{10}$$

A saddle-point splitting of the two branches now results from both the energy gap $E_{tt'}$ between t and t' and the exciton hopping term $\mathcal{J}$. We find virtual extrema of $E_{AD\pm}$ at $Q = 0$ and $\pm Q_0$ where

$$Q_0 = \frac{\sqrt{4G^4 - K^2 E_{tt'}^2}}{2GK} = \frac{E_{tt'}}{2G}\sqrt{\left(\frac{4E_{JT}}{E_{tt'}}\right)^2 - 1} \quad . \tag{11}$$

In the weak coupling limit, $4E_{JT}/E_{tt'} < 1$, the real extrema appear at $Q = 0$ only: an anharmonic well of the upper branch $E_{AD+}(Q)$ and another one of the lower branch $E_{AD-}(Q)$. The excitonic polaron is on- center retaining the particular site symmetry. This harmony is disrupted at strong coupling, $4E_{JT}/E_{tt'} > 1$, and the central extremum of $E_{AD-}(Q)$ turns into a maximum and two lateral wells appear at $\pm Q_0$. The upper branch $E_{AD+}(Q)$ grows steeper but retains a minimum at $Q = 0$. In this coupling range the original symmetry is broken and the exciton becomes off-center to a lower symmetry at $\pm Q_0$. The two branches come as close as $E_{tt'}$ at $Q = 0$. Due to the polaronic effect, the exciton energy is lowered from one of the free exciton bands, of width $\mathcal{J}_t$ or $\mathcal{J}_{t'}$, to an excitonic polaron band of width $\delta\varepsilon_{tt'}$ given by:

$$\delta\varepsilon_{tt'} = \frac{E_{tt'}}{2}\left(1 - \frac{E_{tt'}}{4E_{JT}}\right)\mathrm{cosech}\left\{\frac{2E_{JT}}{\hbar\omega}\left[1 - \left(\frac{E_{tt'}}{4E_{JT}}\right)^2\right]\right\} \tag{12}$$

and centered at an energy ε_P as:

$$\varepsilon_P = \frac{1}{2}\hbar\omega - E_{JT} - \frac{E_{tt'}}{2\left(1 - S_{tt'}^2\right)}\left[\left(1 + S_{tt'}^2\right)\frac{E_{tt'}}{8E_{JT}} - S_{tt'}^2\right] \ , \tag{13}$$

where $S_{tt'} = \exp\{-(2E_{JT}/\hbar\omega)[1-(E_{tt'}/4E_{JT})^2]\}$. One gets the large-radii excitons for $4E_{JT} \sim E_{tt'}$ and small-radius ones for $4E_{JT} >> E_{tt'}$. The vibronic exciton band hosts the hopping between off-center sites.
The above analysis of excitonic polarons amounts to carrying out a renormalization of the exciton Hamiltonian, obtained as:

$$\mathcal{H} = \sum_{(ll')tt's} \mathcal{J}_{ll'}^{tt'} B_{lt}^+ B_{lt'} + \sum_{lts} \varepsilon_{lt} B_{lt}^+ B_{lt} \ , \tag{14}$$

where $\mathcal{J}_{ll'}^{tt'} = \delta\varepsilon_{tt'}/2$ and $\varepsilon_{lt}(s) = E_{lt}(s) + \varepsilon_P$ are the renormalized hopping and single-particle energies, respectively. While the energy lowering tends to stabilize the vibronic exciton, the interwell hopping tends to restore the original site symmetry. Eq.(12) projects an energy gap $E_{tt'}$ onto an off-center polaron hopping band $\delta E_{tt'}$ composed of energy levels from the vibronic mixing of $\mathcal{J}_t$ and $\mathcal{J}_{t'}$. This band is wider for $4E_{JT}/E_{tt'} \geq 1$ close to the onset of an off-center instability. Consequently, a large-radius exciton makes rapid flips between off-centered sites bringing back on the average the original site-symmetry. At $4E_{JT}/E_{tt'} > 1$, $\delta E_{tt'}$ is too narrow to sustain the interwell transfer; so the small-radius vibronic exciton gets immobilized in a lower-symmetry well.

APPLICATION OF EXCITON SELF TRAPPING

Here we consider a special case of exciton self-trapping that leads to the localization of a pair of holes at a chemical bond in semiconductors (9,10). The process leads to the bond-breaking and ejection of atoms from the surface. Also the di-electron localization taking place at Ga dangling bonds is predicted by density functional calculations near adatoms on GaAs surfaces assisted by strong lattice relaxation (11). The combined process may be regarded as an exciton-pair localization.
We consider a two-step localization process in which two holes (or electrons) are trapped at a bond in a sequence. While the first hole stays trapped, the second one experiences a potential $U(r)$ due to the first hole, including the screening effect of the electron-hole atmosphere and the carrier-lattice interaction potential. The potential $U(r)$ is repulsive at long range but attractive at short range, as given below:

$$U(r,Q) = -(GQ + U_0)\left[1 - \Theta(r - r_0 - Q)\right] + \frac{e^2}{\kappa r}\exp\left(-\frac{r}{r_D}\right)\Theta(r - r_0 - Q) \ , \tag{15}$$

where r is the separation between the two holes, r_0 the trapping radius, $\Theta(r)$ the step function, $r_D = \sqrt{ek_BT/8pme^2}$ is Debye's screening radius, κ the dielectric constant and m the free carrier density. Defining an attractive potential U_{eff} between the two holes we can get $U_{eff} = GQ - U_0 = U_0 - E_{LR} < 0$, where U_0 is the Hubbard's repulsive potential. We can now write the Hamiltonian as:

$$H = H_h + H_{ph} + H_{h-ph} \tag{16}$$

$$H_h = \frac{p_h^2}{2m_h} + U(r,0) \tag{17}$$

$$H_{ph} = \frac{P^2}{2M} + \frac{1}{2}KQ^2 \tag{18}$$

$$H_{h-ph} = b(r)Q \tag{19}$$

where $b(r) = \partial U(r,Q)/\partial Q\big|_{Q=0}$ is the hole-phonon coupling coefficient and $K = M\omega^2$ is the mode force constant. For solving Schroedinger's equation with the adiabatic Hamiltonian $H_{AD} \equiv H - P^2/2M$ we choose a basis of two eigenstates of $H_h + H_{h\text{-}ph}$: (i) a free hole state $|k\rangle$ with energy E_k and (ii) a bound state $|b\rangle$ with energy E_b. Thus we get:

$$E_\pm(Q) = \frac{1}{2}\left(H_{bb} + H_{kk} \pm \sqrt{(H_{bb}+H_{kk})^2 + 2|H_{bk}|^2} \right) , \qquad (20)$$

where

$$H_{bb} = \langle b|H_{AD}|b\rangle = \frac{1}{2}K(Q-Q_b)^2 - (E_{LR}-W-U_0) \qquad (21)$$

$$Q_b = -\frac{b_{bb}}{K}, \quad E_{LR} = \frac{1}{2}KQ_b^2 = \frac{b_{bb}^2}{2K}$$

$$H_{kk} = \langle k|H_{AD}|k\rangle = \frac{1}{2}KQ^2 + b_{kk}Q + E_k \qquad (22)$$

$$H_{bk} = H_{kb} = \langle b|H_{AD}|k\rangle = b_{bk}Q \qquad (23)$$

with $b_{bb} = \langle b|b(r)|b\rangle = -G$, $b_{kk} = \langle k|b(r)|k\rangle = 0$, $b_{bk} = \langle b|b(r)|k\rangle = -G\langle b|k\rangle_{\text{in}}$. The bound-state minimum at $Q = Q_b$ in H_{bb} is stabilized by a lattice relaxation energy $E_{LR} = G^2/2K$ and destabilized by the bound hole kinetic energy E_b, roughly equal to the free hole half-bandwidth W, as well as by Hubbard's energy U_0. Since the overlap of a free hole state with the bound hole state is infinitesimally small, the phonon-assisted transition rate, k_{Rk}, from $|k\rangle$ to $|b\rangle$, becomes dominant and is obtained as (12):

$$k_{Rk} = \frac{2}{\hbar^2\omega}\sqrt{\frac{\pi k_B T}{E_{LR}}}\sinh\left(\frac{\hbar\omega}{2k_B T}\right)|H_{bk}(Q_{bk})|^2\exp\left(\frac{E_{bk}}{k_B T}\right) , \qquad (24)$$

where

$$E_{bk} = \frac{1}{2}KQ_{bk} + b_{kk}Q_{bk} = \frac{(W+U_0-E_k)^2}{E_{LR}} .$$

E_{bk} is the crossover barrier between parabolae H_{bb} and H_{kk} relative to the minimum energy, E_k, of H_k. The crossover occurs at Q_{bk}, given by:

$$Q_{bk} = \frac{E_b - E_k}{b_{kk} - b_{bb}} = \frac{W+U_0-E_k}{G} .$$

We sum over the energy in the sea of free hole states (Fig.1), and then the rate in Eq.(24) becomes:

$$k_R = \frac{2}{\hbar^2\omega}\sqrt{\frac{\pi k_B T}{E_{LR}}}\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\sum_{Ek}|H_{bk}(Q_{bk})|^2\exp\left(\frac{E_{bk}}{k_B T}\right) , \qquad (25)$$

where

$$H_{bk} = b_{bk}Q_{bk} = -(W+U_0-E_k)\langle b|k\rangle_{\text{in}} ,$$

and then converting the summation into an integration in Eq.(25) we get:

$$k_R = \frac{2}{\hbar^2\omega}\sqrt{\frac{\pi k_B T}{E_{LR}}}\sinh\left(\frac{\hbar\omega}{2k_B T}\right) \times$$

$$\int|\langle b|k\rangle\langle k|b\rangle|_{\text{in}}(W+U_0-E)^2\exp\left(\frac{-(W+U_0-E)^2}{4E_{LR}k_B T}\right)\rho(E)dE \qquad (26)$$

where $\rho(E)$ is the hole density of states. For a surface, we can set $\rho(E) = N_s/W$, where N_s is the number of surface bonds, and then Eq.(26) becomes:

$$k_R = \frac{2\sqrt{\pi}\, N_s E_{LR} (k_B T)^2}{W \hbar^2 \omega} \left\langle \left| \langle b | k \rangle \langle k | b \rangle \right|_{in} \right\rangle \sinh\left(\frac{\hbar\omega}{2 k_B T}\right) \times$$

$$\times \left\{ u \exp\left(-u^2\right) + \frac{\sqrt{\pi}}{2}\left[1 - F(u)\right] \right\} \quad , \tag{27}$$

where

$$F(u) = \frac{2}{\sqrt{\pi}} \int_0^u \exp\left(-x^2\right) dx, \quad u^2 = \frac{\left(W + U_0\right)^2}{4 E_{LR} k_B T} \quad ,$$

and u^2 is related to the barrier height E_{b0} between free and self-trapped hole states shown in Fig. 1, which is obtained as: $E_{b0} = K Q_{b0}^2/2 = \left(W + U_0\right)^2 / 4 E_{LR}$. At $u \gg 1$ the rate in Eq.(27) is proportional to $\exp(-u^2) = \exp(-E_{b0}/k_B T)$.
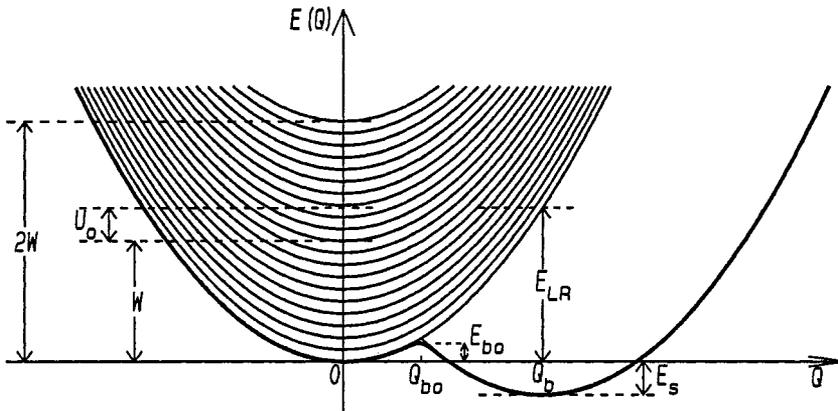
Fig. 1. Adiabatic potentials of the sea of free holes (left) and of the bound hole (right).

ELECTROSTATIC RESPONSE

Another example is the electrostatic response of off-centered vibronic excitons. Previous studies have suggested that exciton pairing may occur via a dipole-dipole coupling (13). Here we show that the exciton pairing may be enhanced by symmetry breaking through off-center displacement, similar to the situation in ammonia molecule (14). The peculiar behaviour of polarons coupled to asymmetric modes has already been suggested by Holstein (8) who found that the coupling to an asymmetric intramolecular vibration could split the vibronic potential double well, which is quite similar to what is found in the theory of the inversion spectrum of the ammonia molecule.

Electric-field coupling

As excitons are polarizable, they may be expected to couple to an external electric field through permanent or induced dipoles. Consider an extra charge e_I, localized at site I, whose interaction energy with a quantized field of small excitons can be written by multipole expansion as:

$$H' = S_{ijvv's} W(i,j|vv')\, B_{ivs}^+ B_{jv's} \quad , \tag{28}$$

where

$$W(ij|vv') = \frac{e_I e}{\kappa} \int \frac{w_v(r - r_i)\, w_{v'}(r - r_j)}{|r - r_I|} dr = U_i\, \delta_{vv'} - p_{ivv'} \cdot F_i \quad , \tag{29}$$

where $U_i = e_I e / \kappa R_i^2$ and $F_i = e_I R_i / \kappa R_i^3$ is the field due to the extra charge. $p_{ivv'}$ is a v-v' mixing dipole:

$$p_{ivv'} = \int w_v^*(u_i)\, e u_i\, w_{v'}(u_i)\, du_i \quad , \tag{30}$$

where $w_v(u)$ are Wannier's functions.

The expectation value of H' in $|AD-;Q\rangle$ state at $E_{AD-}(Q)$ is obtained as:

$$\langle H'_{ii}\rangle \equiv \langle AD-;Q|H'_{ii}|AD-;Q\rangle = -p_{itt'}\cdot F_i\cos(\phi_{itt'}) = -p_{itt'}(Q)\cdot F_i \quad ,$$

where incorporating the adiabatic off-center dipole at Q we get:

$$p_{itt'}(Q) \equiv p_{itti}\cos(\phi_{itt'}) = p_{itt'}\frac{2GQ}{\sqrt{2GQ^2 + E_{tt'}^2}} \quad . \tag{31}$$

Averaging of Eq.(31) over the ground state centered at $\pm Q_0$ gives:

$$\pm p_{itt'}(Q_0) = \pm p_{itt'}\sqrt{1 - \left(\frac{E_{tt'}}{4E_{JT}}\right)^2} \quad . \tag{32}$$

The eigenvalues of the complete vibronic Hamiltonian

$$H_{vib} \equiv H_{vib0} + \langle H'\rangle_0 = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Q^2} + \frac{1}{2}\left(KQ^2 - \sqrt{(2GQ)^2 + E_{tt'}^2}\right) - p_{itt'}(Q_0)\cdot F_i \tag{33}$$

give

$$\delta\varepsilon_{tt'}(F) = \sqrt{\delta\varepsilon_{tt'}^2(0) + \frac{\left(2p_{itt'}(Q_0)\cdot F_i\right)^2}{1-S^2}} \tag{34}$$

and

$$E_p(F) = E_p(0) \quad . \tag{35}$$

Thus the field widens the tunneling splitting $\delta\varepsilon_{tt'}$ but leaves the binding energy $E_p(F)$ unchanged. The field-dependent term in Eq.(34) is a monopole - induced-dipole coupling potential giving rise to a binding energy U_b as:

$$U_b = \frac{1}{4}\left[\delta\varepsilon_{tt'}(F) - \delta\varepsilon_{tt'}(0)\right] \cong \frac{1}{2}\alpha_{vib}F_i^2 \quad , \tag{36}$$

where

$$\alpha_{vib} = \frac{\left[p_{itt'}(Q_0)\cos(p,F)\right]^2}{d\varepsilon_{tt'}(0)} \tag{37}$$

is a renormalized vibronic polarizability (cf. (14,15)).

Dipole-dipole pairing

The exciton-exciton pairing interaction also can be described in a similar way. Defining a pair interaction Hamiltonian as:

$$H'_{ij} = \frac{1}{2}\Sigma_{\alpha\beta\gamma\delta,ijkl}W(\alpha\beta\gamma\delta|ijkl)\ B_{i\alpha s}^+ B_{j\beta s}^+ B_{k\gamma s}B_{l\delta s} \quad , \tag{38}$$

where

$$W(\alpha\beta\gamma\delta|ijkl) = \int\frac{e^2}{\kappa}\frac{w_\alpha^*(r-r_i)w_\beta^*(r'-r_j)w_\gamma(r-r_k)w_\delta(r'-r_l)}{|r-r'|}d^3r\ d^3r'$$

$$= U_{ij}\delta_{\alpha\delta}\delta_{\beta\gamma} + \frac{1}{2\kappa R_{ij}^3}\left(q_{i\alpha\delta}\delta_{\beta\gamma} + q_{j\beta\gamma}\delta_{\alpha\delta} - 2p_{i\alpha\delta}p_{j\beta\gamma}\right) \tag{39}$$

$U_{ij} = e^2/\kappa R_{ij}^2$, $p_{i\alpha\beta} = \langle w_\alpha(u_i)|eu_i|w_\beta(u_i)\rangle$ and $q_{i\alpha\beta} = \langle w_\alpha(u_i)|e^2u_i^2|w_\beta(u_i)\rangle$. Using the symmetry we get $p_{i\alpha\beta} = 0$ ($\alpha = \beta$) and $q_{i\alpha\beta} = 0$ ($\alpha \neq \beta$). Setting $\gamma = \alpha$ and $\delta = \beta$ we get a coupling constant composed of an intraband ($\alpha = \beta$) monopole-monopole interaction and of an interband ($\alpha \neq \beta$) dipole-dipole term. Excitons may pair due to the energy matrix element $W(\alpha\beta\alpha\beta|ijji)$. At ($\alpha \neq \beta$) the corresponding part of H'_{ij} becomes:

$$H'_{ij} = \frac{1}{2}\Sigma_{i\neq j,\alpha\neq\beta}\left(\frac{p_{i\alpha\beta}\cdot p_{j\beta\alpha}}{\kappa R_{ij}^3}B_{i\alpha s}^+ B_{j\beta s}^+ B_{j\alpha s}B_{i\beta s} + \mathrm{h.c.}\right)$$

Adding H_{ij} in the exciton Hamiltonian as:

$$H = \sum_{(ij)\alpha\beta s} T_{ij\alpha\beta s} B^+_{i\alpha s} B_{j\beta s} + \sum_{i\alpha s} E_{i\alpha s} B^+_{i\alpha s} B_{i\alpha s} + H_{ij} \, . \tag{40}$$

we can solve again the Schroedinger's equation similar to Eq.(33) and get a dispersive pairing interaction of excitons with a Van-der-Waals binding energy U_b as:

$$U_b = \frac{E_{\alpha\beta}}{4}\left(\frac{\alpha_{el}}{\kappa_0 R^3_{ij}}\right)^2 \, , \tag{41}$$

which can be renormalized by exciton-phonon coupling, and then we get

$$U_b = \frac{\delta\varepsilon_{ii}}{4}\left(\frac{\alpha_{vib}}{\kappa_0 R^3_{ij}}\right)^2 \, . \tag{42}$$

The effective well-interchange frequency then becomes $\delta\varepsilon_{ii}/2\hbar$.

DIMERS IN LAYERED MATERIALS

The dimer condensation has been observed in materials with conducting planes separated by parallel insulating layers. Highly polarizable off-centered oxygens O(A) of an insulating layer may promote the formation of dimers: excitons or bipolarons. Here we will discuss the Bose condensation and binding energy of dimers.

Bose condensation temperature of 2-D dimers
The Bose-condensation temperature of a gas of noninteracting 2-D dimers of bulk density n_b is usually written as (16,17):

$$T_c = \frac{3.31\hbar^2 n_b^{2/3}}{k_B m_{2D}^{2/3} m_{1D}^{1/3}} \tag{43}$$

where m_{2D} is the transport effective mass. m_{1D} is a c-axis leak effective mass. Here we will present a way to calculate m_{1D} and m_{2D} so that T_c can eventually be calculated. Given the monomer hopping energy, t_m, the dimer hopping term, t_b, is obtained by second-order perturbation from negative-U or small- polaron tight-binding Hamiltonians as $t_b = 4(gt_m)^2/U_b$; U_b is the dimer binding energy, g is the coordination number (18). We get the effective dimer transport mass as:

$$m_{2D} = \frac{\hbar^2}{2t_b d_b^2} = \frac{\hbar^2 U_b}{8\left(gt_m d_b\right)^2} \, , \tag{44}$$

where d_b is the dimer hopping distance.
The leaked mass m_{1D} can be derived by tight-binding arguments using the axial CT energy gap E_{CT}, which is the gap energy of two relevant orbital or hybrid axial states. E_{CT} will couple to the axial stretching modes since they modulate the orbital overlap. A polaron-narrowed CT gap $2t_{1D}$ results as:

$$t_{1D} = E_{JT|CT} \mu_{CT}(1 - \mu_{CT})\mathrm{cosech}\left(u^2_{CT}\right) \tag{45}$$

where $\mu_{CT} = E_{CT}/4E_{JT|CT}$ and $u_{CT} = \sqrt{(2E_{JT|CT}/\hbar\omega_{CT})\sqrt{1-\mu^2_{CT}}}$. $E_{JT|CT} = G_{CT}^2/2K_{CT}$ and $\hbar\omega_{CT}$ are the associated JT energy and bare- phonon frequency, respectively, $K_{CT} = M_{CT}\omega^2_{CT}$ is the force constant of the CT-coupled oscillator with reduced mass M_{CT}. The 1-D hops come across a barrier between two configurational wells separated by $d_{1D} = 2\sqrt{\hbar\omega_{renCT}/K_{CT}}\, u_{CT}$. We get m_{1D} as:

$$m_{1D} = \frac{\hbar^2}{t^2_{1D} d^2_{1D}} \, . \tag{46}$$

Using Eqs.(43-46), the Bose condensation temperature can be calculated.

Binding energy

Assuming that the apical oxygen atom O(A) contributes to the pairing of in-plane carriers we get:

$$U_b = \frac{1}{2}\alpha_{vib}\left(F_1 + F_2\right)\cdot\left(F_1 + F_2\right) \quad , \tag{47}$$

where α_{vib} is the O(A) electrostatic-polarizability tensor and F_i is the electric field produced by the i-th carrier at the apex site.

As O(A) traverses the off-centered volume its polarizability gets modified. Consequently α_{vib} is the polarizability tensor of an off-centered ellipsoid rather than of a single ion. Coupling to A_{2u} bond-stretching yields two off-centered sites along c-axis, and then one gets:

$$\alpha_{zz} = \frac{P_A^2\left(1-\mu_A^2\right)}{3t_A}\left[\tanh\left(\frac{t_A}{k_BT}\right) + \frac{t_A}{k_BT}\text{sech}^2\left(\frac{t_A}{k_BT}\right)\right] \quad ,$$

and coupling to E_u bond-bending yields four off-axis sites in layer as:

$$\alpha_{xx} = \alpha_{yy} = \frac{P_E^2\left(1-\mu_E^2\right)}{3t_E}\frac{\dfrac{t_E}{k_BT}\exp\left(-\dfrac{t_E}{k_BT}\right) + \sinh\left(\dfrac{t_E}{k_BT}\right)}{\exp\left(-\dfrac{t_E}{k_BT}\right) + \cosh\left(\dfrac{t_E}{k_BT}\right)} \quad ,$$

where $P_{A,E}$ are mixing dipoles and $t_{A,E}$ are the tunneling splittings of the transfer between off-center sites. $t_{A,E}$ are like t_{1D} with their respective JT energies, force- and mixing- constants given by:

$$t_{A,E} = E_{JT|A,E}\,\mu_{A,E}(1-\mu_{A,E})\text{cosech}\left(\frac{2E_{JT|A,E}}{\hbar\omega_{A,E}}\sqrt{1-\mu_{A,E}^2}\right) \quad . \tag{48}$$

Using $t_{A,E}$ in Eq.(47) through α_{zz} and α_{xx} we get

$$U_b = \frac{1}{2}\left[\alpha_{xx}\left(F_x^2 + F_y^2\right) + \alpha_{zz}F_z^2\right], \quad F = F_1 + F_2 \quad . \tag{49}$$

Using point-charge electrostatics $F_i = \pm\left(e/R_i^3\right)R_i$, where R_i is the separation between O(A) and the i-th carrier. Writing $F_z = F\cos\varphi$ we get:

$$U_b = \left(\frac{e}{\kappa R^2}\right)^2 \left[1 \pm \cos\left(R_1, R_2\right)\right]\left[\alpha_{xx}\sin^2(\varphi) + \alpha_{zz}\cos^2(\varphi)\right] \quad , \tag{50}$$

where the angle $(R_1, R_2) = \pi - 2\varphi$ for a symmetric geometry with $R_1 = R_2 = R$. We calculate the polarizabilities and minimize $-U_b$ to get:

$$\varphi_{opt} = \sin^{-1}\left(\sqrt{\frac{\alpha_{zz}}{2\left(\alpha_{zz} - \alpha_{xx}\right)}}\right) \quad . \tag{51}$$

We find $\varphi_{opt} \sim \pi/4$ for bihole dimers. There from we compute R and the optimal geometry of a pair. The results of our calculations, using $\kappa = 5$ (16), suggest that both intra- and inter- plane pairing are possible with a hole-mediator separation of ~ 5Å, as shown in Fig.2.
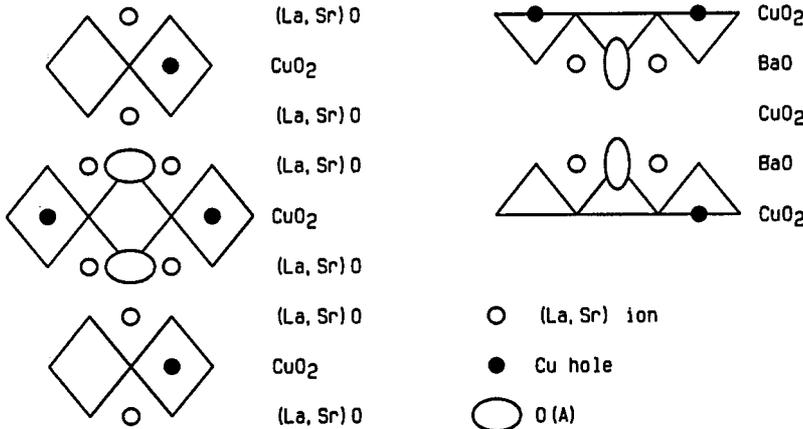
Fig.2.

Likely geometries of intra- and inter-layer hole dimers in high-T_c materials.

T_c-p phase diagrams

To incorporate a dependence on the number of excited electron-hole pairs we note that both the axial hopping energies t_a and t_m should depend on the carrier's density p, since they do so on the plane-to-apex separation r_a, known to shrink as p increases: $t_a \equiv t_a(p) = A/r_a^f$, $t_m(p) = t_m(0) + (dt_m/dr_a)(dr_a/dp)p$ and $r_a \equiv r_a(p) = r_{at}-(r_{at}-r_{ac})p$ where $3 \leq f \leq 4$; r_{at} and r_{ac} relate to the undoped and heavily doped phases respectively. The phase diagrams of non-interacting small bosons are then obtained as (17):

$$T_c(p) = \frac{26.48}{k_B} \frac{\sqrt[3]{\left(N_b P_b\right)^2 d_b^4 \left[g t_m(p)\right]^4 \frac{E_{JT}^2}{K_{CT}}} \times}{\sqrt[3]{p^2 \mu_{CT}(p)\left[1 + \mu_{CT}(p)\right]\left[1-\mu_{CT}(p)\right]^2 \operatorname{cosech}\left(\frac{2E_{JTCT}}{\hbar \omega_{CT}}\sqrt{1-\mu_{CT}^2}\right)U_b^{-2}}} \tag{52}$$

Eq.(52) holds for any mechanism yielding a pairing energy U_b. The polarization model combines it with Eq.(50). U_b being temperature-dependent, Eq.(52) and Eq.(50) comprise a transcendent system to be solved numerically for each T_c, as shown in Fig.3.
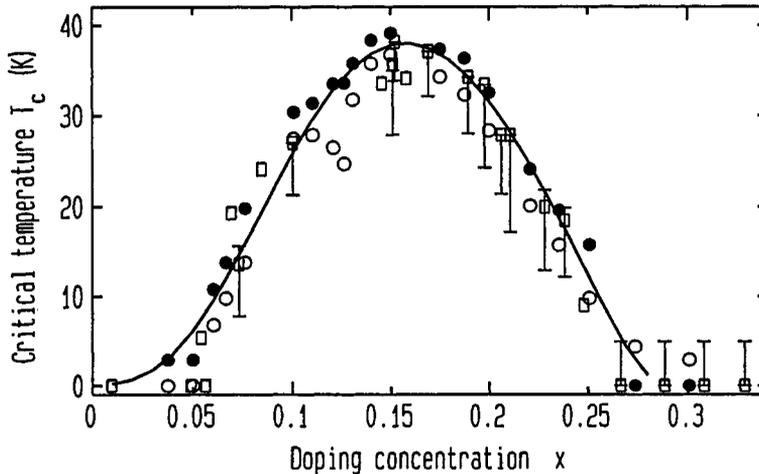
Fig.3. The T_c-x phase diagram of La$_{2-x}$Sr$_x$CuO$_4$.

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