Near-degeneracy of extended \( s + d_{x^2-y^2} \) and \( d_{xy} \) order parameters in quasi-two-dimensional organic superconductors

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The symmetry of the superconducting order parameter in quasi-two-dimensional BEDT-TTF organic superconductors is a subject of ongoing debate. We report \textit{ab initio} density functional theory calculations for a number of organic superconductors containing \( \kappa \)-type layers. Using projective Wannier functions we derive parameters of a common low-energy Hamiltonian based on individual BEDT-TTF molecular orbitals. In a random phase approximation spin-fluctuation approach we investigate the evolution of the superconducting pairing symmetry within this model and point out a phase-transition between extended \( s + d_{x^2-y^2} \) and \( d_{xy} \) symmetry. We discuss the origin of the mixed order parameter and the relation between the realistic molecule description and the widely used dimer approximation. Based on our \textit{ab initio} calculations we position the investigated materials in the obtained molecule model phase diagram and simulate scanning tunneling spectroscopy experiments for selected cases. Our calculations show that many \( \kappa \)-type materials lie close to the phase transition line between the two pairing symmetry types found in our calculation, possibly explaining the multitude of contradictory experiments in this field.

I. INTRODUCTION

Quasi-two-dimensional organic charge transfer salts of bis-ethylenedithio-tetrathiafulvalene molecules, abbreviated BEDT-TTF or ET, have attracted much interest due to their rich phase diagram\([1,2]\). Among these materials, the family of \( \kappa \)-(ET)\(_2\)X salts, where \( \kappa \) refers to a specific arrangement of the ET molecules and X corresponds to a monovalent anion, stands out due to the realization of fascinating states of matter like Mott insulator, unconventional superconductor or spin-liquid\([3,4]\). Especially the immediate vicinity of the superconducting phase to an antiferromagnetic Mott insulator suggests a deeper connection between two-dimensional orbitals and high-temperature cuprate superconductors\([5,6]\).

Although superconducting \( \kappa \)-type charge transfer salts have been investigated, for instance, in studies of specific heat\([7,8]\), surface impedance\([9]\), thermal conductivity\([10]\), millimeter-wave transmission\([11]\), scanning tunneling spectroscopy (STS)\([12,13]\) and elastic constant\([14]\), no consensus about the symmetry of the superconducting pairing has been reached so far. Some of the experiments are in favor of \( s \)-wave symmetry\([15,16]\), while other studies have proposed \( d \)-wave states with contradictory positions of the nodes in the superconducting order parameter\([17,18]\). Evidence for a mixed-symmetry order parameter was recently provided in Refs.\([19,20]\). Notably, evidence for a phase separation between different \( d \)-wave states has recently been reported in Ref.\([18]\).

In theoretical approaches, the \( \kappa \)-(ET)\(_2\)X family of materials is often described by a half-filled Hubbard model of (ET)\(_2\) dimers on the anisotropic triangular lattice\([21,22]\), which is equivalent to a square lattice model with an additional coupling along one of the diagonals. Many theoretical methods have been applied to the dimer based Hubbard model, for instance, the fluctuation-exchange approximation (FLEX)\([23,24]\), the path-integral renormalization group\([25]\), cluster dynamical mean field theory\([26,27]\), variational Monte Carlo\([28,29]\) and exact diagonalization\([30,31]\). These studies do not agree entirely on all details of the phase diagram, especially whether superconductivity is realized in the model or not. Those studies that do show superconductivity nevertheless agree, with the exception of Ref.\([20]\), that it is of \( d_{x^2-y^2} \)-type as in high-temperature cuprate superconductors\([32]\).

Although the triangular lattice Hubbard model has been remarkably successful in explaining the overall phase diagram\([21,22]\) and also some more subtle physics of \( \kappa \)-(ET)\(_2\)X materials, the recent discovery of multiferroic\([33]\) in antiferromagnetic \( \kappa \)-(ET)\(_2\)Cu[N(CN)\(_2\)]Cl and the still unresolved problem of superconducting coupling-symmetry\([34,35]\), call for alternative approaches. In particular, the dimer model on the anisotropic triangular lattice is only an approximation with \textit{a priori} unclear range of applicability to the real lattice structure of \( \kappa \)-(ET)\(_2\)X charge transfer salts. In a seminal paper\([36]\), Kuroki et al. investigated the superconducting pairing taking into account the realistic lattice structure and in fact found a phase transition between \( d_{x^2-y^2} \)- and \( d_{xy} \)-symmetric states when lowering the degree of dimerization. Other possible directions of future theoretical research beyond the dimer Hubbard model are outlined in Refs.\([37,38]\).

In this work, building upon the idea by Kuroki et al., we derive a set of realistic molecule-based low-energy models for superconducting \( \kappa \)-(ET)\(_2\)X materials from \textit{ab initio} density functional theory (DFT) calculations. After identifying the parameter region relevant for the real materials, we investigate the symmetry of the superconducting pairing in this model within a random phase approximation (RPA) spin-fluctuation approach. Our results show that the position of many materials in the phase diagram is close to a phase-transition line between states with extended \( s + d_{x^2-y^2} \) and \( d_{xy} \) pairing symmetry. Furthermore, we clarify that the customary dimer
The dimer model not only fails in the limit of weak dimerization, but also when the in-plane anisotropy of hopping integrals becomes too large, which we find to be the case for all investigated materials. Finally, we simulate tunneling spectra in the superconducting state for selected cases and compare our findings to relevant experiments.

II. METHODS AND MODELS

A. Ab-initio calculations and model Hamiltonian

We use ab initio density functional theory (DFT) calculations within an all-electron full-potential local orbital (FPLO)\textsuperscript{52} basis to calculate the electronic bandstructure. For the exchange-correlation functional we employ the generalized gradient approximation (GGA)\textsuperscript{53}. All calculations are converged on $6 \times 6 \times 6$ $k$-point grids. We use crystal structures from Refs. \textsuperscript{54} \textsuperscript{56} In the case of Ref. \textsuperscript{56} where crystal structures were measured for several temperatures, we use the data taken at 100 K.

In contrast to the customary dimer approximation, we model the $\kappa$-(ET)$_2$ layer taking into account each individual ET molecule as a lattice site (see Fig. 1). Tight-binding parameters are obtained from projective molecular orbital Wannier functions as implemented in FPLO\textsuperscript{52}. Therefore, the number of bands in the tight-binding model is equal to the number of ET molecules in the crystallographic unit cell. With the molecular Wannier function method, almost perfect representations of the DFT bandstructures can be obtained and ambiguities from fitting procedures are avoided. The latter is especially important for many-body calculations based on the obtained low-energy Hamiltonians.

In the following model investigation, we only keep the four largest in-plane hopping elements $(t_1,t_2,t_3,t_4)$ between ET molecules [see Fig. 1(a)]. The resulting hopping structure is a generalization of the Shastry-Sutherland lattice\textsuperscript{55}, which is reached in the limit of $t_2 = t_4$ and $t_3 = 0$. In cases where the unit cell contains multiple $\kappa$-type layers, we discard all but one of the layers after the Wannierization procedure, because the interlayer coupling is negligible. In some of the investigated compounds, the crystal symmetry is lowered with respect to the high-symmetry orthorhombic space group $Pnma$ of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br, which leads to a small additional splitting of the hoppings $t_i$ into $t_i$ and $t'_i$. For simplicity, this particular anisotropy is discarded in our study by averaging the hopping integrals as $t_i = (t_i + t'_i)/2$. As a result, we obtain the kinetic part of a four-band Hamiltonian which is $3/4$-filled and of the same form for all materials investigated.

$$H_0 = \sum_{ij\sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.)$$ \hspace{1cm} (1)

Alternatively, because ET molecules in $\kappa$-type arrangement are quite strongly dimerized, it is popular to approximate the $\kappa$-(ET)$_2$ layer by dimers on an anisotropic triangular lattice, integrating out the intra-dimer degrees of freedom. The parameters of this dimer model can be calculated directly from the molecule model using geometric formulas\textsuperscript{21}

$$t = \frac{(|t_2| + |t_4|)}{2} \hspace{1cm} (2a)$$

$$t' = \frac{|t_3|}{2} \hspace{1cm} (2b)$$

By convention the dimer approximation uses the crystallographic unit cell containing two dimers [see Fig. 1(b)]. Therefore, the dimer-approximated Hamiltonian consists of two bands, which are half-filled. Note that based on the geometric formulas, any anisotropy between $t_2$ and $t_4$ of the molecule model is discarded when going from the molecule to the dimer model. With few exception\textsuperscript{55} the dimer approximated model nevertheless reproduces well the low-energy part of the original bandstructure. It has recently been demonstrated that improved estimates for dimer model parameters can be obtained by a Wannier function calculation\textsuperscript{55}.

The two-band dimer model can be unfolded to a one-band model by transforming to a unit cell of half the size and rotated by 45 degrees. The so-obtained model is directly related to the square lattice Hubbard model, but with an additional coupling along one of the diagonals. Results obtained in the one-band model are therefore rotated by 45 degrees with respect to the physical Brillouin zone of organic charge transfer salts, so that e.g. different $d$-wave order parameters exchange their designation when going from one to the other Brillouin zone (see Fig. 2). Thus, the same physical order parameter which has $d_{xy}$-symmetry in the realistic four molecule/two dimer unit cell [Fig. 2(b)] has $d_{x^2-y^2}$-symmetry in the model one dimer/one band unit cell.
FIG. 2. (Color online) (a) The inner bold lines show Brillouin zone and Fermi surface of a generic \( \kappa \)-\( (ET)_2X \) material. The outer dashed lines show Brillouin zone and Fermi surface of the unfolded one-band dimer model. (b) \( d_{xy} \) order parameter in the physical Brillouin zone. Nodes are located in the \( x \) - and \( y \) -directions. (c) \( d_{x^2-y^2} \) order parameter in the unfolded Brillouin zone. Nodes are located along the Brillouin zone diagonals. The different designation is only due to a rotation of the coordinate axes by 45°. (d) \( d_{x^2-y^2} \) order parameter in the physical Brillouin zone. (e) \( d_{xy} \) order parameter in the unfolded Brillouin zone.

In our study, we always work in the physical unit cell containing two dimers [Fig. 2(b) and (d)]. We refer to the small backfolded part of the Fermi surface close to the Brillouin zone boundary as the elliptic part of the Fermi surface, while we call those sheets running almost parallel to the \( k_y \)-direction quasi-1D.

An overview of unit cell and hopping paths for molecule and dimer model is shown in Fig. 1. The resulting Hamiltonians in orbital-space for all three cases are listed in appendix A.

B. RPA spin-fluctuation calculations

In \( \kappa \)-(ET)\(_2\)X materials there is strong evidence for antiferromagnetic spin-fluctuation\(^{60}\). Therefore, we investigate the superconducting state of these materials based on a random phase approximation (RPA) spin-fluctuation approach in the singlet channel\(^{61,62}\). We have extended our implementation from single-site multi-orbital models\(^{63,64}\) to multi-site single-orbital models relevant for the materials discussed here. Compared to the FLEX approximation used in Ref. 17, our RPA method uses only states at the Fermi level and neglects the electronic self-energy correction. While this approximation prevents us from making quantitative statements about the superconducting transition temperature \( T_c \), it reduces significantly the numerical cost compared to FLEX, so that we can calculate the momentum structure of the superconducting order parameter for numerous input parameter sets and with high angular resolution. Competing magnetically ordered or paramagnetic Mott insulating states are not investigated in our study. Furthermore, we do not investigate possible time-reversal symmetry-breaking superconducting states or spin-triplet pairing.

The low-energy Hamiltonian is given by the kinetic part \( H_0 \), derived with the Wannier function method described above, and the intra-orbital Hubbard interaction \( H_{\text{int}} \).

\[
H = H_0 + H_{\text{int}} = \sum_{ij\sigma} t_{ij}(c_{i\sigma}c_{j\sigma} + h.c.) + U/2 \sum_{i\sigma} n_{i\sigma} n_{i\overline{\sigma}} \quad (3)
\]

Here, \( \sigma \) represents the spin and \( n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \). The sum over \( i \) runs over all ET sites in the unit cell. The interaction strength \( U \) is treated as a parameter. Note that the Coulomb repulsion on a dimer and the Coulomb repulsion on a molecule are not identical. Especially the role of intermolecular Coulomb repulsion is currently unclear. The investigation of interaction terms beyond on-site repulsion is left for future studies.

We calculate the non-interacting static susceptibility \( \chi^0 \), where matrix elements \( a_{\mu}^\dagger(\vec{k}) \) resulting from the diagonalization of the initial Hamiltonian \( H_0 \) connect orbital and band space denoted by indices \( l \) and \( \mu \) respectively. The \( E_{\mu} \) are the eigenvalues of \( H_0 \) and \( f(E) \) is the Fermi function. \( N \) is the number of sites in the unit cell.

\[
\chi^0_{l_1 \ldots l_k \mu_1 \ldots \mu_k}(\vec{q}) = -\frac{1}{N} \sum_{\vec{k},\mu,\nu} a_{\mu}^\dagger(\vec{k})a_{\nu}^\dagger(\vec{k})a_{\nu}(\vec{k}+\vec{q})a_{\mu}(\vec{k}+\vec{q}) f(E_{\mu}(\vec{k}+\vec{q})) - f(E_{\nu}(\vec{k}+\vec{q})) = -\frac{1}{E_{\nu}(\vec{k}+\vec{q}) - E_{\mu}(\vec{k})}
\]

(4)

In our calculation both \( \vec{q} \) and \( \vec{k} \) run over uniform grids spanning the reciprocal unit cell. Temperature enters the calculation through the Fermi functions.

The fraction in Eq. (4) becomes problematic in numerical calculations, when the band energies \( E_{\nu} \) and \( E_{\mu} \) become degenerate. However, the expression can be rectified using l’Hospital’s rule, which we use in practice when the magnitude of the denominator falls below a certain threshold (e.g. \( 10^{-7} \) eV). Here, \( \beta \) denotes the inverse temperature \( \beta = (k_B T)^{-1} \).

\[
\lim_{E_{\nu} \to E_{\mu}} \frac{f(E_{\nu}(\vec{k}+\vec{q})) - f(E_{\mu}(\vec{k}))}{E_{\nu}(\vec{k}+\vec{q}) - E_{\mu}(\vec{k})} = -\beta \frac{e^{\beta E_{\mu}}}{(e^{\beta E_{\mu}} + 1)^2} \quad (5)
\]

The static spin- and orbital-susceptibilities \( \chi^s_{\text{RPA}} \) and \( \chi^c_{\text{RPA}} \) are constructed in an RPA framework. Since the interaction term defined in Eq. (3) is local and we have
only one orbital per lattice site, we can restrict the calculation to the diagonal elements of the susceptibility and use scalar equations for the RPA-enhanced susceptibilities.

\[
\chi_{L}^{+,\text{RPA}}(\vec{q}) = \frac{\chi_{L}^{0}(\vec{q})}{1 - U\chi_{L}^{0}(\vec{q})} \quad (6a) \\
\chi_{L}^{-,\text{RPA}}(\vec{q}) = \frac{\chi_{L}^{0}(\vec{q})}{1 + U\chi_{L}^{0}(\vec{q})} \quad (6b)
\]

Here, \(\chi_{L}\) with \(L = \{llll\}\) denotes the diagonal element of the susceptibility tensor associated with an ET site indexed by \(l\). Note that this formulation allows us to treat multiple inequivalent ET sites in the unit cell, keeping the individual \(\vec{q}\)-dependence of their associated susceptibilities. Therefore, the symmetry of the susceptibility follows the symmetry of the ET layer in the crystallographic unit cell, which is important for checking the simplified four-parameter model against \(ab\) \textit{initio} Hamiltonians, which can have monoclinic, as e.g. in \(\kappa-(ET)_{2}\text{Cu(NCS)}_{2}\), or even triclinic symmetry, as in \(\kappa-\alpha'_{1}-(ET)_{2}\text{Ag(CF}_{3}\text{)}_{4}(\text{TCE})\).

The total spin susceptibility is given by the sum over all site-resolved contributions:

\[
\chi^{s}(\vec{q}) = \frac{1}{2} \sum_{L} \chi_{L}^{+,\text{RPA}}(\vec{q}) \quad (7)
\]

The pairing vertex in orbital space for the spin-singlet channel can be calculated using the fluctuation exchange approximation\footnote{\textsuperscript{[5-7]}}:

\[
\Gamma_{l_{1}l_{2}l_{3}l_{4}}(\vec{k},\vec{k}') = \left[ \frac{3}{2} U\chi^{+,\text{RPA}}(\vec{k} - \vec{k}')U \right] - \frac{1}{2} U\chi^{-,\text{RPA}}(\vec{k} - \vec{k}')U + U \int_{l_{1}l_{2}l_{3}l_{4}} \quad (8)
\]

In the pairing vertex, the momenta \(\vec{k}\) and \(\vec{k}'\) are restricted to the Fermi surface. As vectors \(\vec{k} - \vec{k}'\) do not necessarily lie on the grid used in the calculation of the susceptibility \(\chi^{0}(\vec{q})\), we interpolate the grid data linearly.

The pairing vertex in orbital space is transformed into band space using the matrix elements \(a_{\mu}^{\dagger}(\vec{k})\):

\[
\Gamma_{\mu\nu}(\vec{k},\vec{k}') = \text{Re} \sum_{l_{1}l_{2}l_{3}l_{4}} a_{\mu}^{\dagger}(\vec{k})a_{\nu}^{\dagger}(\vec{k}') \left[ \Gamma_{l_{1}l_{2}l_{3}l_{4}}(\vec{k},\vec{k}') \right] \times a_{\nu}^{\dagger}(\vec{k}')a_{\mu}(\vec{k}) \quad (9)
\]

Finally, we solve the linearized gap equation by performing an eigendecomposition on the kernel and obtain the dimensionless pairing strength \(\lambda_{i}\) and the symmetry function \(g_{i}(\vec{k})\).

\[
- \sum_{\nu} \int_{C_{\nu}} \frac{d\vec{k}'}{2\pi} \frac{1}{2\pi v_{F}(\vec{k}')} \left[ \Gamma_{\mu\nu}(\vec{k},\vec{k}') \right] g_{\nu}(\vec{k}') = \lambda_{i}g_{i}(\vec{k}) \quad (10)
\]

The integration runs over the discretized Fermi surface and \(v_{F}(\vec{k})\) is the magnitude of the Fermi velocity.

For the computations presented in this paper, we evaluated the susceptibility \(\chi^{0}(\vec{q})\) using \(50 \times 50\) point grids for \(\vec{q}\) and the integrated-out variable \(\vec{k}\) (see Eq. \(4\)). The inverse temperature in the susceptibility calculation is fixed to \(\beta = 160/\ell_{1}\) for the molecule model and \(\beta = 60/\ell_{1}\) for the dimer model. These values result in about the same effective temperature. The Fermi surface is determined by inverting linear interpolants for the band energies on a fine grid. For the models considered here about 250 points on the Fermi surface are sufficient. The Hubbard repulsion parameter \(U\) is chosen in all calculations so that the leading eigenvalue in Eq. \(10\) is \(\lambda = 0.99 \pm 0.001\). For most combinations of input parameters this leads to a clear separation of the leading and the first subleading eigenvalue. The pairing symmetries corresponding to the leading and sub-leading eigenvalues do not change as a function of \(U\).

C. Simulation of tunneling spectra in the superconducting state

The central quantity measured in the scanning tunneling spectroscopy (STS) experiments on superconductors is the local density of states (DOS) in the superconducting phase. Here we start from the standard Bardeen-Cooper-Schrieffer (BCS) theory for isotropic s-wave superconductors. A simple approximate extension allows us to treat realistic Fermi surfaces and unconventional pairing symmetries derived from the \(ab\) \textit{initio} calculations combined with RPA spin-fluctuation theory as presented above.

To derive an approximation for the DOS of a superconductor, we start with the Hamiltonian for Cooper pairs with vanishing total momentum\footnote{\textsuperscript{[7]}}:

\[
H = \sum_{k,\sigma} \epsilon_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k,k'} U(k,k')c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger c_{-k'\downarrow} c_{k'\uparrow} \quad (11)
\]

The interaction can be treated in mean field theory \((\delta(c_{\uparrow}c_{\downarrow}^\dagger} = c_{\uparrow}c_{\downarrow} + \langle c_{\uparrow}c_{\downarrow}^\dagger \rangle)\), where terms quadratic in \(\delta\) are neglected. The resulting Hamiltonian can be diagonalized using the Bogoliubov-Valatin transformation which introduces quasiparticle creation and annihilation operators \(\gamma_{k\sigma}^\dagger\) and \(\gamma_{k\sigma}\). The quasiparticle excitation energies are given as \(E_{k} = \sqrt{\epsilon_{k}^{2} + 2|\Delta_{k}|^{2}}\), where \(\Delta(k) = \sum_{k'} U(k,k')c_{-k'\downarrow}^\dagger c_{k'\uparrow}\).

The BCS Hamiltonian can be rewritten in terms of the quasiparticle creation and annihilation operators:

\[
H_{\text{BCS}} = \sum_{k,\sigma} E_{k} \gamma_{k\sigma}^\dagger \gamma_{k\sigma} + \sum_{k} \epsilon_{k} c_{k\uparrow}^\dagger c_{k\downarrow} - \sum_{k,k'} U(k,k')(c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger)(c_{-k'\downarrow} c_{k'\uparrow}) \quad (12)
\]

The excitation spectrum of the quasiparticles \(E_{k}\) is gapped and defined only for positive energies. The density of states of quasiparticles in an isotropic s-wave superconductor can be calculated from the normal state
The quasiparticle DOS \( \rho_{\text{qp}}(E) \) is the constant superconducting gap \( \Delta_\mathbf{k} = \Delta \):

\[
\rho_{\text{qp}}(E) = \frac{1}{\pi} \sum_\mathbf{k} \delta(E - E_\mathbf{k}) = \int dE \rho_0(E) \frac{\left\langle \epsilon^2 + |\Delta_\mathbf{k}|^2 \right\rangle}{\sqrt{E^2 - |\Delta|^2}} \\
= \left\{ \begin{array}{ll} 
\rho_0(\sqrt{E^2 - |\Delta|^2}) \frac{E}{\sqrt{E^2 - |\Delta|^2}} & E > |\Delta| \\
0 & E < |\Delta| \end{array} \right.
\]

The previous derivation assumed an isotropic gap and an energy dispersion of free electrons to identify the normal state DOS \( \rho_0 \). For realistic electronic structure and anisotropic gap \( \Delta_\mathbf{k} \) this factorization of contributions is not easily possible due to the non-trivial momentum dependence of both functions:

\[
\rho_{\text{qp}}(E) = \int dE \rho_0(E) \frac{\left\langle \epsilon^2 + |\Delta_\mathbf{k}|^2 \right\rangle}{\sqrt{E^2 - |\Delta|^2}} \\
\neq \int dE \rho_N(E) \delta(|E| - \sqrt{\epsilon^2 + |\Delta_\mathbf{k}|^2})
\]

However, in a widely used ansatz \[63\,89\] the electrons with effective mass \( m^* \) are considered to be free, i.e., the Fermi surface is approximated by a concentric circle, and the gap only depends on the angle \( \theta \).

\[
\rho_{\text{qp}}(E) \approx \frac{1}{(2\pi)^2} m^* \text{Re} \int d\theta \frac{|E|}{E^2 - |\Delta(\theta)|^2}
\]

We introduce in this expression a finite quasiparticle lifetime \[70\] by adding an imaginary part \( \Gamma \) to the quasiparticle excitation energies. This allows us to carry out calculations with finite angular resolution and facilitates comparison to experiment. Furthermore, we improve upon the circular integration by replacing it with a summation over the discretized realistic Fermi surface and drop the irrelevant prefactors to obtain the final expression for the quasiparticle DOS in our study:

\[
\rho_{\text{qp}}(E) \propto \sum_\mathbf{k} \text{Re} \frac{|E + i\Gamma|}{\sqrt{(E + i\Gamma)^2 - \Delta(\mathbf{k})^2}}
\]
We observe that all materials fall into a narrow region of parameters: \( t_1 \in [165,190] \) meV, \( t_2 \in [95.6,119] \) meV, \( t_3 \in [52.2,82.4] \) meV and \( t_4 \in [17.3,36.3] \) meV. Normalizing \( t_2, t_3 \) and \( t_4 \) with respect to \( t_1 \), this means all materials lie in the range \( t_2/t_1 \in [0.538,0.661], t_3/t_1 \in [0.289,0.404] \) and \( t_4/t_1 \in [0.099,0.220] \). Note the pronounced anisotropy between \( t_2 \) and \( t_4 \). These intervals of \( t_2/t_1, t_3/t_1 \) and \( t_4/t_1 \) obtained from the ab initio calculations determine the parameter ranges for our following model investigation.

We sorted the materials according to their superconducting transition temperature \( T_c \), but we found no correlation of \( T_c \) with either \( t_1, t_2, t_3 \) or \( t_4 \). The ratios \( t_2/t_1, t_3/t_1 \) or \( t_4/t_1 \) are also not obviously connected to \( T_c \).

B. Pairing symmetry in the dimer model

First, we apply the RPA spin-fluctuation formalism to the dimer model in the range \( t'/t \in [0,1] \). We evaluate the superconducting order parameter in fine steps of \( t'/t \) and compare the leading eigenfunctions. In all cases we find that a \( d_{xy} \)-state is the leading pairing symmetry.

Relating the dimer model back to the one-band model explained in the methods section, the \( d_{xy} \)-state we find is identical to the \( d_{x^2-y^2} \)-state of the square lattice Hubbard model after unfolding the Brillouin zone (see Fig. 2).

Typical superconducting \( \kappa \)-(ET)$_2$X materials lie in the region \( t'/t \lesssim 0.65 \), where a \( d_{xy} \)-solution is to be expected, as the dimer model is basically a square lattice of hoppings \( t \), perturbed by the additional diagonal coupling \( t' \). The diagonal coupling \( t' \) breaks the \( C_4 \)-symmetry of the underlying square lattice and gives the Fermi surface its elliptic shape, but the dominant terms in the Hamiltonian remain square lattice-like. For a full account of possible pairing symmetries in the one-band Hubbard model on the square lattice, see Ref. 75.

An early theoretical study of the antiferromagnetic phase of \( \kappa \)-type materials concluded that the two molecules within a dimer carry the same spin and that the spins are flipped between neighboring dimers, giving rise to \( (\pi,\pi) \) magnetic order as in the parent compounds of high-temperature cuprate superconductors. This result is consistent with our observation that a dimerized model gives a \( d_{xy} \) order parameter in the physical Brillouin zone, which becomes a \( d_{x^2-y^2} \)-symmetry in the unfolded zone of the one-band model (see Fig. 2), again emphasizing the deep connection between cuprates and quasi-two-dimensional organic superconductors.

We would also like to note that the authors of Ref. 13, referring to the physical Brillouin zone, invoked a \( d_{xy} \) superconducting symmetry close to insulating patches and a \( d_{x^2-y^2} \) state in the bulk to explain the findings of their STS study on deuterated \( \kappa \)-(ET)$_2$Cu[N(CN)$_2$]Br. As the antiferromagnetic insulating state is dimerized (see Ref. 22), the dimer approximation naturally applies and gives a \( d_{xy} \) order parameter in accordance with the experimental observation. What remains to be answered in an approach beyond the dimer model, as presented in the next sections, is why the superconducting order parameter of the bulk is \( d_{x^2-y^2} \).

C. Pairing symmetry in the molecule model

The obvious step for going beyond the dimer model is to use the original crystal lattice, i.e. the molecule model explained above (see Fig. 1). In order to compare the results of the molecule model to those of the dimer model we do the following consideration: via the geometric Eq. 2, the four-parameter molecule model is mapped onto a two-parameter dimer model. With this procedure we are left with two adjustable parameters in the molecule model whose variation discloses important features of the systems, not captured in the resulting dimer model which remains unchanged. These adjustable parameters are: the degree of dimerization \( t_1/\max(t_2, t_3, t_4) \) and the in-plane anisotropy \( t_4/t_2 \).

The degree of dimerization obviously decides whether the dimer approximation applies to a material or not. Its influence on the superconducting pairing was quantified by Kuroki et al., who found a transition to a \( d_{x^2-y^2} \) state in the physical Brillouin zone at low dimerization (see Ref. 47).

Less obvious is how this \( d_{x^2-y^2} \) state emerges from the underlying hopping structure and how important the anisotropy between \( t_2 \) and \( t_4 \) is for the pairing state. To investigate these issues, we construct a series of molecule models with fixed value of \( t_3/t_1 = 0.333 \) and vary the ratio \( t_4/t_2 \) in the range \([0,1]\) (for the values realized in real materials see Table I). We fix the sum of \( t_2 \) and \( t_4 \) so that the molecule models correspond to the same dimer model \( t_3/(t_2 + t_4) = t'/t = 0.6 \). The maximum value of \( t_2 \) is therefore \( t_2^{\max} = 0.556 \) and its minimum value is \( t_2^{\min} = 0.278 \). As \( t_4 \) is increased, the in-plane anisotropy decreases and the dimerization defined as \( t_1/\max(t_2, t_3, t_4) \) increases.

In Fig. 3 we show the spin susceptibilities and leading pairing symmetries in the molecule model as a function of \( t_4/t_2 \) compared to the associated dimer model. In the isotropic limit \( t_4/t_2 = 1 \) we find a \( d_{xy} \)-symmetric state, similar to the one found in the dimer model [compare Fig. 3(d) and Fig. 3(e)]. Upon lowering \( t_4/t_2 \) the maximum of the superconducting gap shift toward the position where the nodes in a \( d_{xy} \)-symmetric state are and additional nodes appear on the quasi-1D part of the Fermi surface close to (\( \pm x, 0 \)). As this shift is equivalent to a rotation by 45 degrees, the state with eight nodes can be expected to have significant \( d_{x^2-y^2} \) contribution. In the limit of \( t_4 \ll t_2 \) the additional set of nodes on the quasi-1D part of the Fermi surface vanishes [see Fig. 3(a)].

The remaining four nodes are situated close to the Brillouin zone boundary, where the smaller elliptic part of the Fermi surface is folded back. The details of the pairing symmetry are discussed further below. In what follows we investigate the origin of the gap maxima shifts.
As an example we show in Fig. 4 how extrema of the gap magnitude with opposite sign appear where parts of the Fermi surface can be connected by a wave-vector $\vec{q}$ that shows a peak in the spin susceptibility. Note that in Fig. 3 the Brillouin zone is shifted by a vector $(\pi, \pi)$, because the relevant vectors $\vec{q}$ connect pieces of the Fermi surface across the boundaries of the Brillouin zone used in Fig. 3.

Now we come back to the discussion of the results presented in Fig. 3. At $t_4/t_2 = 0$ peaks appear at $\vec{q}_1 \approx (\pm 0.7 \pi, 0)$ and $\vec{q}_2 \approx (\pm \pi/2, \pm \pi)$, the dominant contribution to the spin susceptibility being the peak at $\vec{q}_2$. As $t_4/t_2$ is increased, the position of $\vec{q}_1$ remains about the same, while $\vec{q}_2$ shifts towards $(\pm \pi/4, \pm \pi/2)$ and decreases in intensity. At $t_4/t_2 = 1$, the peak at $\vec{q}_1$ becomes the dominant contribution to the spin susceptibility. As we do not work in the limit of infinite dimerization, even the case $t_4/t_2 = 1$ does not reproduce the dimer model spin susceptibility exactly. The similarities are however apparent.

These peak shifts in the spin susceptibility are reflected in the pairing symmetry: the gap maxima of different sign in the $d_{xy}$-symmetry are separated by a wave-vector $\vec{q}_1$, while $\vec{q}_2$ is responsible for the sign change between the upper and lower half of the elliptic Fermi surface. Furthermore, $\vec{q}_2$ enforces an enlarged nodal region close to $(\pm \pi, 0)$, since it would otherwise connect parts of the Fermi surface with the same sign of the gap. In the intermediate region of $t_4/t_2$, $\vec{q}_2$ connects the 1D parts of the Fermi surface, where it induces an additional set of nodes. The large gap on the elliptic part of the Fermi surface is connected to the 1D sheets by $\vec{q}_1$. The shift of the vertical lines in the susceptibility, which widen towards $k_x \approx \pm \pi/2$, merely reflect the changing shape of the Fermi surface. For $t_4 \ll t_2$ the additional set of nodes on the 1D sheets vanishes, because they are no longer connected by $\vec{q}_2$, which now instead points from 1D sheet to the elliptic parts just like $\vec{q}_1$. This consideration shows that the pairing-symmetry transition in the molecule model is driven by a peculiar competition between $\vec{q}_1$ and $\vec{q}_2$ nesting vectors.

Now we connect the structure of the susceptibility and the superconducting pairing to the underlying lattice model. The feature at $\vec{q}_1$ is obviously connected to the $t_3$ hopping parameter, since it is the only hopping exclusively in $\pi$-direction (compare Fig. 1). All other $t$-parameters can only be responsible for a four-peak structure, as they occur pointing along both diagonals of the physical unit cell. The influence of the competition between $t_2$, $t_3$ and $t_4$ on the feature at $\vec{q}_2$ is however hard to quantify directly. Therefore, we decompose the superconducting order parameter in terms of extended $s$- and $d$-wave basis functions $f_i$ appropriate for a square lattice geometry. For each of the $d$-wave basis functions, we also take into account the associated extended $s$-wave function, because we expect that a significant extended $s$-wave component could mix with the $d$-wave states to accomodate the orthorhombicity of the model:

$$f_{s_1}(\vec{k}) = \cos k_x + \cos k_y$$

(17a)

$$f_{d_{x^2-y^2}}(\vec{k}) = \cos k_x - \cos k_y$$

(17b)

$$f_{s_2}(\vec{k}) = \cos k_x \cdot \cos k_y$$

(17c)

$$f_{d_{xy}}(\vec{k}) = \sin k_x \cdot \sin k_y$$

(17d)

Rotated into the Brillouin zone of $\kappa$-type materials, gap functions $f_{d_{xy}}$ and $f_{s_2}$ are to be expected from antiferro-
magnetic exchange along square-like bonds \( (t_2, t_4) \), while \( f_s \) and \( f_{d_{x^2-y^2}} \) correspond to exchange paths along diagonal bonds \( (t_3) \), see Fig. 5.

We fit the pairing symmetries calculated from RPA to a linear combination of the previously defined pairing symmetries and determine their relative contributions \( c_i \).

\[
\tilde{g}(\vec{k}) = c_{s_1} f_s + c_{d_{x^2-y^2}} f_{d_{x^2-y^2}} + c_{s_2} f_{s_2} + c_{d_{xy}} f_{d_{xy}} \tag{18}
\]

For the \( d_{xy} \)-state we find \( c_{d_{xy}} = 1 \) and all other contributions zero, i.e. except for the not well reproduced extended nodal region close to \((\pm \pi, 0)\) the dimer model and the molecule model at \( t_4/t_2 \lesssim 1 \) are dominated by the square-lattice physics of \( t \) and \( t_2, t_4 \) respectively. For the \( d_{x^2-y^2} \)-like solution at \( t_4 \ll t_2 \) we find negligible contributions from \( f_s \) and \( f_{d_{xy}} \), dominant \( f_{s_2} \) and sub-dominant \( f_{d_{x^2-y^2}} \). For increasing \( t_4/t_2 \) the ratio of coefficients \( c_{d_{x^2-y^2}} / c_{s_2} \) decreases, i.e. the square-lattice physics becomes dominant when the asymmetry between \( t_2 \) and \( t_4 \) is removed. Using the symmetry functions \( f_i \), all details of the superconducting gap in the \( d_{x^2-y^2} \)-like state including the additional nodes can be reproduced by Eq. 18.

Our findings provide a clear picture of the pairing competition in the molecule model: in the realistic region of parameters, where the dimerization measured by \( t_1/\max(t_2, t_3, t_4) \) and the anisotropy of \( t_2 \) and \( t_4 \) are finite, the competition of square-like \( (t_2, t_4) \) and diagonal \( (t_3) \) hopping realizes a unique linear combination of functions \( f_{d_{x^2-y^2}} \) and \( f_{s_2} \) as the leading pairing symmetry. We refer to this linear combination as \( s_+ + d_{x^2-y^2} \), or extended \( s + d_{x^2-y^2} \). The \( s \)-wave contribution is equivalent to the \( s_\pm \) pairing state believed to be realized in iron-based superconductors (see e.g. Ref. 72) and has been overlooked entirely in the literature on quasi-two-dimensional organic charge transfer salts. When the lattice becomes more square-like \( (t_4 \lesssim t_2) \), i.e. the molecule model approaches the dimer limit, the \( d_{xy} \)-symmetry known from the dimer model takes over. In other words, in the context of realistic modelling of \( \kappa \)-type materials, the \( d_{xy} \) symmetry found in the dimer model \( (d_{x^2-y^2} \) in the unfolded one-band model) is mostly an artifact of the underlying approximation to the real lattice structure (Eq. 2).

Finally, we checked our results obtained with the four parameter molecule model against the original hopping structure obtained from projective Wannier functions, which includes longer range processes. As expected, the differences induced by the distance cutoff and parameter averaging are negligible.

### D. Pairing symmetry phase diagram of the molecule model

To complete our study of the pairing symmetry competition, we investigated the leading pairing symmetry of the molecule model as a function of \( t_2/t_1, t_3/t_1 \) and \( t_4/t_1 \) in the range of parameters realized in actual superconducting \( \kappa \)-type materials.

In Fig. 5, we show the obtained phase diagram, which consists of a \( d_{xy} \)-symmetric phase at low \( t_2/t_1 \) and \( t_3/t_1 \),...
while the rest of the phase diagram shows a $s_{\pm} + d_{x^2-y^2}$ state. The consecutively numbered symbols in Fig. 6 correspond to the position of real materials as listed in Table I within this phase diagram. As we scanned the phase diagram several times for different fixed $t_4/t_1$, materials were sorted into the cut with the closest value of $t_4/t_1$.

At low $t_2/t_1$ the phase boundary is almost horizontal, i.e. independent of the precise value of $t_2/t_1$. For larger values of $t_2/t_1$ the model becomes more asymmetric with respect to $t_2$ and $t_4$ and a smaller diagonal coupling $t_3$ is sufficient to drive the system into the $s_{\pm} + d_{x^2-y^2}$ state. The size of the $d_{xy}$-symmetric region is obviously determined by the value of $t_4/t_1$ as explained in the previous section.

In the numerical calculations we observed that the leading two pairing symmetries are almost degenerate in a broad parameter region. This is to be expected, because the $s_{\pm} + d_{x^2-y^2}$ state emerges precisely as a compromise between two different nesting vectors, of which one rather fits to a pure $d_{xy}$-symmetry. To clarify this degeneracy, we calculated the eigenvalues of the leading and sub-leading solutions of the gap equation at fixed $t_2/t_1$ and $t_3/t_1$ and varied $t_4/t_2$ in the range $[0,1]$. Fig. 7 shows the eigenvalues of both possible pairing states as a function of the in-plane anisotropy $t_4/t_2$. We observe a pronounced asymmetry: While the $d_{xy}$-state is competitive even for low values of $t_4/t_2$, the $s_{\pm} + d_{x^2-y^2}$ quickly becomes irrelevant when approaching the isotropic case ($t_4/t_2 = 1$).

Finally, based on our parameter estimates, all materials investigated lie in the $s_{\pm} + d_{x^2-y^2}$ region of the phase diagram. Materials particularly close to the phase transition line are $\kappa$-(ET)$_2$I$_3$, $\kappa$-(ET)$_2$Ag(CN)$_2$-H$_2$O and $\kappa$-(ET)$_2$Cu[N(CN)$_2$][Br. These can be expected to realize the $s_{\pm} + d_{x^2-y^2}$ order parameter with eight nodes. Evidence for eight node mixed-symmetry superconductivity has recently been found in Ref. 19.

When materials are close to the phase transition line, small changes of the hopping parameters might drive them into the $d_{xy}$ state, which is always present as a sub-dominant pairing symmetry. For such local changes of parameters, for instance lattice defect or disorder of molecular conformations could be responsible. In Ref. 18 we have shown that different conformations of ET molecules result in decidedly different ratios of $t_4/t_2$. The degree of conformational disorder can be controlled experimentally by adjusting the sample cooling rate.

In Ref. 22 a square lattice-like antiferromagnetic order was found for the insulating state of $\kappa$-type materials. Therefore, we expect significant competition between antiferromagnetism and $d_{xy}$-symmetric superconductivity, while the $s + d_{x^2-y^2}$-symmetric state is realized farther away from the magnetically ordered insulating phase. Within this picture, recent results by Oka et al. interpreted their experiment in terms of patches with a $d_{xy}$ order parameter and a $d_{x^2-y^2}$-symmetric bulk, can be qualitatively explained.

At this point we would like to point out that most
experimental studies assume a four-node $d$-wave order parameter upon data analysis, which excludes from the start the detection of the $s_\pm$-component we found. In particular, the realization of the $s_\pm + d_{x^2-y^2}$ state with eight nodes which lie along the diagonals and close to the crystallographic axes, may explain the considerable disagreement in the experimental literature regarding the node positions.

E. Simulation of scanning tunneling spectroscopy

Most transport experiments on $\kappa$-(ET)$_2$X materials have proven to be difficult to interpret and could not resolve the symmetry of the superconducting pairing so far. However, recent improvements in sample preparation for low-temperature scanning tunneling spectroscopy (STS) experiments have allowed for progress towards a resolution of the superconducting order parameters.

Therefore, in this section we simulate tunneling spectra in the superconducting state for molecule model parameters $t_2/t_1 = 0.4375$, $t_4/t_1 = 0.1$ and various values of $t_3/t_1$: a four-node $s_\pm + d_{x^2-y^2}$ state is obtained for $t_3/t_1 = 0.5$, an eight-node $s_\pm + d_{x^2-y^2}$ state for $t_3/t_1 = 0.3475$ and $d_{xy}$ for $t_3/t_1 = 0.25$. We employ the representation of the superconducting gap in terms of symmetry functions introduced in Eq. [18] which we multiply with a prefactor $\Delta_0 = 10$ meV to obtain a spectrum with reasonable energy scale. The gap on the Fermi surface is then given by $\Delta(\vec{k}) = \Delta_0 \tilde{g}(\vec{k})$. We use this expression together with Eq. [19] to calculate the quasiparticle density of states $\rho_{qp}$, which corresponds to the local density of states (LDOS) observed in STS experiments. The finite quasiparticle lifetime is modelled by $\Gamma = 0.07$ meV.
In the \( d_{xy} \) case we ignore the small anisotropy found in the RPA calculation.

In Fig. 8 we show (i) the obtained gap on the Fermi surface, (ii) the magnitude of the gap versus angle measured from the \( k_x \)-direction and (iii) the simulated tunneling spectrum for the three cases investigated.

The magnitude of the gap versus the angle is distributed anisotropically on the Fermi surface [Fig. 8(a-c) top panel]. Maxima of the gap magnitude are indicated by arrows labelled with capital letters, while nodes in the gap are indicated by arrows labelled with greek letters. The global maximum of the gap magnitude (labelled A or D) resides in all cases on the elliptic part of the Fermi surface, while the second largest maximum (labelled B or E) is located on the quasi-one-dimensional part. A third smallest maximum (labelled C) is possible on the quasi-1D sheet. In the \( d_{xy} \)-case the nodes labelled \( \gamma \) appear in addition to the expected set of nodes \( \delta \), because the Fermi surface touches the Brillouin zone boundary. The \( \gamma \)-nodes lead to the second maximum (labelled E) of the gap magnitude [Fig. 8(a-c) middle panel], but are otherwise irrelevant for the low-energy physics. As the three possible gap structures share two maxima of slightly different size, the simulated quasiparticle DOS looks quite generic [Fig. 8(a-c) bottom panel]. A two-peak structure is observed far away from the Fermi level, which corresponds to the energy values of the two largest maxima in the gap magnitude.

Important differences are however revealed at low energies: the \( d_{xy} \)-state is featurelessly V-shaped [Fig. 8(c) bottom panel], while the spectrum of the eight-node state has an additional peak close to 2 meV [Fig. 8(b) bottom panel], which is linked to the small gap (labelled C) on the quasi-1D sheet. This leads to an outer and an inner V-shape with different slopes. For the four-node \( s_{\pm}+d_{x^2−y^2} \)-state we observe a peculiar dip around 1 meV in the quasiparticle spectrum [Fig. 8(a) bottom panel]. This corresponds to the minimum value of the gap magnitude on the quasi-one-dimensional part of the Fermi surface. Inside of this dip a V-shaped region emerging from the \( \beta \)-nodes is again observed.

We emphasize that our predictions are to be taken as qualitative, not quantitative, regarding the overall energy scale and the relative gap sizes. The main features explained above are however robust. The detection of such low-energy structures is certainly not an easy task, but we believe it will be possible with state-of-the-art equipment and proper sample preparation.

**IV. CONCLUSIONS**

In summary, we investigated the superconducting state of \( \kappa-(ET)_2X \) charge transfer salts in an individual molecule model based on a combination of \textit{ab initio} density functional theory and random phase approximation spin-fluctuation calculations. We obtained kinetic parameters of the molecule Hamiltonian for eight superconducting \( \kappa \)-type materials using projective Wannier functions. We found that the superconducting order parameter in a realistic molecule model is different from the one in the usual dimer approximated Hamiltonian for all investigated materials. The superconducting phase diagram of the molecule description is dominated by an extended \( s+d_{x^2−y^2} \)-symmetry that emerges from the competition between square-like and diagonal hopping processes on the original \( \kappa \)-type lattice, while the physics of the dimer model is reproduced also for finite dimerization in the limit of isotropic parameters \( t_4 \lesssim t_2 \). The anisotropy of square-like isotropic parameters \( t_2 \) and \( t_4 \) is however not negligible in real materials. For precisely this reason, the dimer approximation does not apply to superconducting \( \kappa-(ET)_2X \) charge transfer salts. It overestimates the importance of square lattice physics through the averaging contained in the geometric formulas, which are exact only in the limit of infinite dimerization.

Furthermore, the \( s_{\pm}+d_{x^2−y^2} \)-state, which features nodes both along the crystallographic axes and the Brillouin zone diagonals, might explain the multitude of contradictory experimental results regarding the nodal positions. We also simulated tunneling spectroscopy experiments for all nodal configurations encountered in our phase diagram. The difference between those pairing states unfortunately manifests itself only at very low energies, making experimental detection difficult, but not impossible. Based on the \textit{ab initio} calculated model parameters we found that the well-studied material \( \kappa-(ET)_2Cu[N(CN)_2]Br \) is situated near the phase transition line between \( s_{\pm}+d_{x^2−y^2} \) and \( d_{xy} \) superconducting states, which supports the interpretation of recent scanning tunneling spectroscopy experiments.

A question unanswered by our study is why superconducting transition temperatures among quasi-two-dimensional charge transfer salts can differ by more than a factor of four. As there is no obvious connection between \( T_c \) and the parameters of the kinetic Hamiltonian, a method that can qualitatively reproduce the ordering of transition temperatures in real materials is required to elucidate this issue.

In conclusion we believe that a significant part of the physics in quasi-two-dimensional charge transfer salts has unfortunately been overlooked so far, because theory has adhered to the dimer model for too long and too many experiments have been interpreted based on a dichotomy of \( d_{xy} \) and \( d_{x^2−y^2} \) states, which is inappropriate for the orthorhombic lattice realized in \( \kappa-(ET)_2X \) materials.

It is an interesting open question, whether the magnetic, insulating and possible quantum spin-liquid states known from the anisotropic triangular lattice are also present in the molecule model. The investigation of these phases is left for future studies.
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Appendix A: Matrix elements of the kinetic Hamiltonians

For completeness we list the kinetic part of the dimer model in one- and two-band representation, as well as the kinetic part of the four-band molecule model. We denote the unit cell parameters in x- and y-direction as a and b respectively. The multi-band Hamiltonians are given as matrix elements \( \langle i | H_{\text{hop}} | j \rangle \), where states \( |i\rangle \) denote the orbitals living on a dimer/molecule with site index \( i \). Only unique matrix elements are listed. The rest of the elements are generated by using \( \langle i | H_{\text{hop}} | j \rangle = \langle j | H_{\text{hop}} | i \rangle^\dagger \). In all models there is only one orbital per lattice site.

To obtain the correct electron filling, one has to introduce a chemical potential \( \mu \), so that \( H_0 = H_{\text{hop}} - \mu \sum_{\sigma} c_{i\sigma}^\dagger c_{i\sigma} \) is half-filled for the dimer model in either representation and 3/4-filled for the molecule model.

The single-band representation of the dimer model is given by:

\[
H_{\text{hop}}(\vec{k}) = 2t \left[ \cos(x_a) + \cos(k_y b) \right] + 2t' \left[ \cos(x_a) \cos(k_y b) - \sin(x_a) \sin(k_y b) \right]
\]

(A1)

The two-band representation of the dimer model can be written as:

\[
\langle 0 | H_{\text{hop}} | 0 \rangle = \langle 1 | H_{\text{hop}} | 1 \rangle = 2t' \cos(x_a)
\]

(A2a)

\[
\langle 0 | H_{\text{hop}} | 1 \rangle = 2t \left( 1 + e^{ik_x a} + e^{ik_y b} + e^{ik_x a} e^{ik_y b} \right)
\]

(A2b)

The four-band molecule model is given by:

\[
\langle 0 | H_{\text{hop}} | 1 \rangle = t_1 + t_3 e^{ik_x a}
\]

(A3a)

\[
\langle 0 | H_{\text{hop}} | 2 \rangle = t_4 \left( 1 + e^{-ik_x b} \right)
\]

(A3b)

\[
\langle 0 | H_{\text{hop}} | 3 \rangle = t_2 \left( 1 + e^{-ik_x a} \right)
\]

(A3c)

\[
\langle 1 | H_{\text{hop}} | 2 \rangle = t_2 e^{-ik_y b} \left( 1 + e^{-ik_x a} \right)
\]

(A3d)

\[
\langle 1 | H_{\text{hop}} | 3 \rangle = t_4 e^{-ik_x a} \left( 1 + e^{-ik_y b} \right)
\]

(A3e)

\[
\langle 2 | H_{\text{hop}} | 3 \rangle = t_1 + t_3 e^{-ik_x a}
\]

(A3f)

Here, diagonal entries \( \langle i | H_{\text{hop}} | i \rangle \) are zero for all \( i \).
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