Novel Coexisting Density Wave Ground State in Strongly Correlated, Two-Dimensional Electronic Materials

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Two-dimensional (2D) strongly correlated electron systems underlie many of the most important phenomena in contemporary condensed matter physics, including the Quantum Hall Effect (QHE) [1], “high $T_c$” superconductivity [2], and possible exotic conducting states in silicon MOS-FETs [3]. We demonstrate the existence of yet another exotic ground state in strongly correlated, 2D electronic materials: a novel, insulating bond-order/charge density wave state (BCDW) in the commensurate 1/4-filled band that persists for all anisotropies within the 2D lattice, in contradiction to the non-interacting electron prediction of the vanishing of density waves in 2D for non-1/2-filled bands. The persistence of the BCDW in the 2D lattice is a consequence of strong electron-electron (e-e) interaction and the resultant “confinement,” a concept recently widely debated [4]. Our results have implications for experiments in the organic charge transfer solids (CTS), where they explain the observation of a “mysterious” coexistence of density waves [5,6], clarify the optical conductivity of the “metallic” state [7], and suggest an approach to the observed organic superconductivity.

We consider a 2D lattice, consisting of coupled chains of strongly correlated electrons, described by the quasi-2D extended Peierls-Hubbard Hamiltonian

$$H = H_0 + H_{ee} + H_{inter} \quad (1a)$$

$$H_0 = -\sum_{j,m,\sigma} [t - \alpha(\Delta_{j,m})] B_{j,m+1,m,\sigma} + \beta \sum_{j,m} v_{j,m} n_{j,m}$$

$$+ K_1/2 \sum_{j,m} (\Delta_{j,m})^2 + K_2/2 \sum_{j,m} v_{j,m}^2 \quad (1b)$$

$$H_{ee} = U \sum_{j,m} n_{j,m\uparrow} n_{j,m\downarrow} + V \sum_{j,m} n_{j,m} n_{j+1,m} \quad (1c)$$

$$H_{inter} = -t_\perp \sum_{j,m,\sigma} B_{j,m,m+1,\sigma} \quad (1d)$$

In the above, $j$ is a site index, $m$ is a chain index, $\sigma$ is spin, and we assume a rectangular lattice [8]. As $t_\perp$ varies from 0 to $t$, the electronic properties vary from quasi-1D to quasi-2D, modeling a wide range of materials. Each site is occupied by a molecular unit, the displacement of which from equilibrium is described by $u_{j,m}$ (with $\Delta_{j,m} = (u_{j,m} - u_{j+1,m})$), $v_{j,m}$ is an intramolecular vibration, and $B_{j,k,l,m,\sigma} \equiv [c_{j,k,l,m,\sigma}^c c_{k,l,m,\sigma} + h.c.]$, where $c_{j,k,l,m,\sigma}$ is a Fermion operator. We treat the phonons in the adiabatic approximation and are interested in unconditional broken symmetry solutions that occur for electron-phonon (e-ph) couplings ($\alpha, \beta \rightarrow 0^+$). Although we limit our explicit analysis of e-e interactions to on-site repulsions $U$ and intrachain nearest-neighbour interaction $V$ only, we will find that additional intersite interactions will further stabilize the BCDW.

For the 1/2-filled band, the difference between 1D and 2D is well understood and profound. In the 1D limit, widely discussed for polyacetylene [9], the ground state for physically relevant values of $U > 2V > 0$ is a bond-order wave (BOW), with $u_j = (-1)^j u_0$. In the isotropic 2D limit, which has been applied to the parent compounds of the high $T_c$ superconductors, the ground state for the same physically relevant parameters is an antiferromagnet (AFM, i.e., a 2kF SDW) [10]. Thus in the 1/2-filled band, the dominant broken symmetry depends very strongly on dimensionality and (a) there is no coexistence between the BOW and the SDW; and (b) the strength of the SDW increases monotonically with the interchain hopping.

In contrast to the 1/2-filled band, broken symmetries in non-1/2-filled commensurate correlated bands have been investigated chiefly in the quasi-1D regime, $t_\perp \ll t$, and have employed primarily Fermi surface/”k”-space arguments, which imply that finite $t_\perp$ destroys the Fermi surface nesting that characterises the 1D limit, leading necessarily within the simplest k-space interpretation to the restoration of the metallic phase [11]. The nesting concept, however, is provably applicable only in the limit of zero e-e interactions. For strongly interacting electrons, broken spatial symmetries are more naturally studied by “configuration space” arguments [12]. Using such arguments, we show below that the ground state of Eq. (1) is a novel BCDW state that persists for all $t_\perp$ for the strongly interacting regime $U \geq 4|t|$, provided that the nearest-neighbour Coulomb interaction $V < V_c$, where $V_c = 2|t|$ in the limit $U \rightarrow \infty$ and is slightly larger for finite $U$. For small $t_\perp$,
the BCDW state drives a SDW (creating a “BCSDW”, [13]), but the SDW amplitude, after reaching a maximum, vanishes as \( t_{\perp} \) is further increased. The persistence of the BCDW to the isotropic 2D limit, its coexistence with the SDW for small (but nonzero) \( t_{\perp} \), and the vanishing of the SDW at large \( t_{\perp} \), are all new results, quite unexpected from established behavior of the 1/2-filled band.

We begin with the physical intuition suggesting the existence of the 2D BCDW and the peculiar behavior of the spins. For the 1D 1/4-filled band, Hubbard [13] showed that for large \( U \) and in the presence of long-range Coulomb interactions, there exist two distinct Wigner crystals, represented by the configuration space \( t = 0 \) “cartoons” as \( ...1100... \) and \( ...1010... \), where the numbers denote electron site occupancies (for finite hopping, \( 1(0) \) actually represents site occupancy \( 0.5 + \epsilon \) \((0.5 - \epsilon)\), with \( \epsilon \) small but nonzero). Ref. [16] showed that long-range Coulomb interactions are not essential for the Wigner crystal \( ...1100... \) : this ground state is also obtained for the 1D limit of Eq. (1), provided \( V < V_c \); only for \( V > V_c \) does the Wigner crystal \( ...1010... \) become the ground state [13]. Importantly, for nonzero \( \alpha \) or \( \beta \), this \( ...1100... \) ground state is a coexisting BOW-CDW [10], i.e., BCDW, as indicated by the individual chains in Fig. 1. The bonds in the 1D limit are singlets, but as \( t_{\perp} \) is gradually increased, the sites acquire spins [13], as indicated in Fig. 1. The spin arrangement along a chain is explained by inspection of the 1D Wigner crystal cartoon \( ...1100... \); each ‘0’ is closer to a specific ‘1’, and therefore for finite hopping acquires the same sign (though not magnitude) of the spin density as the site with larger charge density (since it is the same electron that is shared between these two sites). Our detailed numerical calculations show that a \( \pi \)-phase shift between chains gives the lowest electronic energy, implying the structure shown in Fig. 1 for the \( t_{\perp} \ll |t| \) limit. In this Figure, the modulations of the hopping integrals are determined by \( u_{j,m} = U_0(-1)^m r_2 \cos(2k_F j - \pi/4) + r_4 \cos(4k_F j) \), where \( r_2 \) and \( r_4 \) are the amplitudes of the 2k\(_F\) and 4k\(_F\) distortions of \( u_{j,m} \), respectively. Our many-body calculations show that this leads to intrachain CDW \( \rho_c(j) \equiv \langle \sum_{\sigma} c_{j,t}^\dagger c_{j,t+\sigma} \rangle = 0.5 + \rho_0 \cos(2k_F j - 3\pi/4), \) SDW \( \rho_s(j) \equiv \langle c_{j,t}^\dagger c_{j+1,t} - c_{j,t}^\dagger c_{j+1,t+1} \rangle = \rho_{s2} \cos(2k_F j - \pi/4) + \rho_{s4} \cos(4k_F j - \pi) \), and BOW \( \langle \sum_{\sigma} B_{j,j+1,m,m',\sigma} \rangle = b_0 + b_2 \cos(2k_F j - \pi/2) + b_4 \cos(4k_F j - \pi) \) where the phase angles of the DW’s correspond to odd \( m \), and their amplitudes depend on \( U, V \), and \( t_{\perp} \).

We now discuss the consequences of increasing \( t_{\perp} \) further. Interchain hopping \( t_{\perp} \) leads to partial double occupancy on a single site (\( \uparrow \downarrow \) \() with an energy barrier that, while less than the bare \( U \), is a \( U_{eff} \) that increases with \( U \). For large enough \( U_{eff} \), the electrons are thus confined to their respective chains, and the BCDW state persists up to the isotropic 2D limit for the strongly correlated case. A striking feature of the BCDW state is that it is a Wigner crystal along the chains (\( ...1100... \), periodicity 2\( k_F \)), transverse to the chains (\( ...1010... \), periodicity 4\( k_F \)), as well as along both diagonal directions (\( ...1100... \), periodicity 2\( k_F \)). The BCDW state is thus a particularly robust broken symmetry [8]. For instance, by enhancing the 4\( k_F \) charge order along the transverse direction, \( V_{\perp} \) enhances the stability of the BCDW. Similarly, the diagonal \( ...1100... \) charge ordering implies that even the additions of hopping \( t_{\text{diag}} \) and Coulomb repulsion \( V_{\text{diag}} \) along the diagonals will not destroy the Wigner crystal for realistic parameters (in particular, \( V_{\text{diag}} \) stabilizes the BCDW relative to the Wigner crystal that is \( ...1010... \) along both \( x \) and \( y \) directions).

We next describe the evolution of the spin structure. From the cartoon in Fig. 1, we see that for the SDW to exist it is essential that the ‘0’s have spin. In the small \( t_{\perp} \) case, the sign of the spin on a ‘0’ is necessarily that of the nearest intrachain ‘1’. Note, however, that each ‘0’ also has an interchain ‘1’ as a neighbour and that for a stable SDW the spin densities of the ‘1’s that are neighbours of a specific ‘0’ must be opposite. Therefore, with increasing \( t_{\perp} \), competing effects occur. On the one hand, the magnitude of the interchain exchange coupling \( \sim t_{\perp}^2/U_{eff} \) increases. On the other hand, the spin density on a site labeled ‘0’ decreases because of the cancelling effects of the intra- and inter-chain neighbouring ‘1’s. We thus expect the SDW to vanish at a \( t_{\perp}^* \) that will depend on the magnitudes of the bare \( U \) and \( V \).

To confirm these expectations we use exact diagonalization and constrained path quantum Monte Carlo (CPMC) [7] numerical techniques to calculate for representative finite 2D lattices: (i) the electronic energy gained upon bond distortion, \( \Delta E \equiv E(0) - E(u_{j,m}) \), where \( E(u_{j,m}) \) is the electronic energy per site with fixed
distortion $u_{j,m}$ along the chains; (ii) site charge densities $n_j$ and intrachain bond orders ($\sum_\sigma B_{j,j+1,m,m,\sigma}$); and (iii) the $z$-$z$ component of the spin-spin correlations, for each $U$, $V$ and $t_\perp$. A decreasing $\Delta E$ as a function of $t_\perp$ signals the destruction of the distortion by two-dimensionality, while a constant or increasing $\Delta E$ indicates a persistent distortion. In order to determine the correct behaviour in the thermodynamic limit from finite-size simulations, we choose lattices and boundary conditions based on the physical requirement that any nonzero $t_\perp$ must destabilise the BCDW for noninteracting electrons on that particular finite lattice (see supplementary information). We have studied both $r_4 = 0$ and $r_4 = r_2$ (see supplementary information), establishing that while the magnitude of $\Delta E$ does depend on $r_4/r_2$, its behaviour as a function of $t_\perp$ does not, provided only that $r_2 \neq 0$. For brevity we present here the results for $r_4 = 0$ only. We note that the magnitudes of $\Delta E$ for the noninteracting and the interacting cases are very different: Coulomb interactions reduce the $\Delta E_0 \equiv \Delta E |_{t_\perp=0}$ considerably. However, this merely indicates that for a given e-ph interaction the magnitude of the distortion is less for correlated electrons than for noninteracting electrons. Since, however, the interacting single chain is distorted, and since our interest lies in determining the behaviour as a function of $t_\perp$ only, the relevant quantity is not the absolute value of $\Delta E$ but the normalised energy gained per site upon distortion, i.e., $\Delta E/\Delta E_0$. This argument is similar to that made by Anderson for perturbative treatments of coupled chains, viz., the sequence in which the intrachain Coulomb interactions and interchain hopping are included is important, and a correct physical picture is obtained only by first including the Coulomb interactions.

In Fig. 2(a) we compare the behaviour of $\Delta E/\Delta E_0$ for the non-interacting and interacting ($U = 6|t|$; $V = |t|$) cases for three different lattices satisfying our boundary condition constraints. Finite 4n-electron 1D periodic rings have a strong tendency to have total spin $S = 1$ for nonzero U. In the present case, the 8-site periodic ring is $S = 1$ in both the undistorted and distorted states, but the 16-site ring is $S = 1$ in the undistorted state and $S = 0$ when distorted. The $\Delta E_0$ for the $8 \times 2$ and $8 \times 6$ then correspond to the energy gained upon distortion by the 1D $S = 1$ state. This is appropriate, since the ground states of the $8 \times 2$ lattice are $S = 0$ for the smallest nonzero $t_\perp$, and as seen in Fig. 2(a), the exact $\Delta E$ for this case converges smoothly to the $\Delta E_0$ at $t_\perp \to 0$ (the exact diagonalizations here included calculations for $t_\perp$ as small as 0.01). For the $16 \times 6$ lattice, the one-electron orbital occupancy at $U = 0$ is degenerate even for the distorted state in the region $t_\perp > 0.6$ indicating that the distorted state ground state is $S = 1$ for large $t_\perp$ and nonzero U. The calculated $\Delta E$ for the $16 \times 6$ are therefore compared to the triplet $\Delta E_0$ in the region $t_\perp > 0.6$.

![Fig. 2](image)

As seen in Fig. 2(a), while for the non-interacting cases the $\Delta E/\Delta E_0$ decreases rapidly with $t_\perp$, for the interacting cases the $\Delta E/\Delta E_0$ either remains unchanged or is enhanced by $t_\perp$. In Fig. 2(b) we show the charge densities on the sites along a chain for the bond-distorted $8 \times 6$ lattice, for different $t_\perp$ and the same $U$ and $V$ as in (a).

In Fig. 3 we show the interchain spin-spin correlations for the distorted $8 \times 6$ lattice for several values of $t_\perp$. The spin-spin correlations indicate a SDW that is enhanced between $t_\perp = 0.1$ and 0.4 but then vanishes at $t_\perp \approx 0.6$. We observe this same behaviour of the SDW on $8 \times 2$ and the $16 \times 6$ lattices. In all cases, the SDW amplitude initially increases, exhibits a maximum, and then vanishes at a $t_\perp^*$ which decreases with the size of the system. The initial increase of the SDW amplitude indicates that...
$t^*_\perp$ is nonzero, a conclusion that is also in agreement with the experimental observation of the BCSDW state in the weakly 2D organic CTS [5,6]. Based on the calculations for 16 × 6 lattice, we estimate 0.1 < $t^*_\perp$ < 0.3. Theoretically, the 2D BCDW introduces a new mechanism for broken symmetry in strongly correlated lattice systems. The persistence of the BCDW state at large $t^*_\perp$ is related to the Wigner crystal-like charge arrangement along all possible directions. Indeed, our 1/4-filled BCDW state is remarkably similar to the “paired electron crystal” state found in the continuum electron gas by Moulopoulos and Ashcroft [13].

Experimentally, organic CTS, which span the range $t^*_\perp$ ≤ 0.1t in (TMTTF)$_2$X to $t^*_\perp$ ~ t in certain (BEDT-TTF)$_2$X, provide a critical testing ground for our results. First, the 1/4-filled band and the resulting coexistence between the BCDW and the SDW at small $t^*_\perp$ provide a natural explanation [3,4] for the otherwise “mysterious” coexisting CDW/SDW state that has been observed in (TMTSF)$_2$PF$_6$ and (TMTTF)$_2$Br [3] and likely also in α-(BEDT-TTF)$_2$MHg(SCN)$_4$ [1]. Second, recent data [7] on frequency-dependent optical conductivity in the high temperature “metallic” phase of (TMTSF)$_2$ClO$_4$ and (TMTSF)$_2$PF$_6$ exhibit both zero- and finite-energy modes, with the zero-energy mode having a spectral weight of only about 1%. Assuming that the (TMTSF)$_2$X are weakly incommensurate [7], our BCDW state provides a natural explanation, with the zero-energy mode ascribed to the conductivity of the incommensurate defects and the gap mode to the excitation across the BCDW pseudogap that persists at high temperature due to fluctuations associated with low dimensionality.

What might be the relation of our new BCDW state to organic superconductivity, the mechanism for which remains unclear despite two decades of research? Experimentally, in the (TMTSF)$_2$X, the BCSDW state for small $t^*_\perp$ gives way to superconductivity under pressure [9]. Insulator-superconductor transition has also been noted in the BEDT class of materials, where superconductivity is often obtained by slight modifications of the anion (for instance, α-(BEDT-TTF)$_2$M$\text{Hg(SCN)}_4$ are BCSDW for $M$ = K, Rb and Tl, while the $M$ = NH$_4$ compound is superconducting; κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X is an antiferromagnetic semiconductor for X = Cl, but X = Br is superconducting) [21]. Although the “paired” Wigner crystal in the 2D electron gas remains to be proved and is presently controversial [3], it is intriguing that the BCDW state found here is obtained naturally within the standard microscopic lattice Hamiltonian for organic CTS. Several features of our results support the above speculation about the insulator-superconductor transition. First, the vanishing of the SDW and the persistence of the BCDW, taken together, suggest the possibility of singlet coupling between the sites labeled ‘1’ in Fig. 1 in this region, leading to a spin gap. Second, within many existing models of superconducting pairing involving correlated electrons, the interactions that bind two particles often also lead to phase segregation. In contrast, any binding of commensurability defects here would be a consequence of the “quasi-chemical bonding” that occurs between the “occupied” sites, and these pairs are already separated. Finally, our preliminary calculations in the region $t^*_\perp$ > $t^*_\perp$ in small lattices show signatures of superconducting pairing correlations (see supplementary information), but these calculations will have to be extended to larger lattices before firm conclusions can be drawn.
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