

## Extended Hubbard model of superconductivity and charge-density-waves in the layered 2H transition metal dichalcogenides

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Based on an extended Hubbard model and a simplified version of the fluctuation exchange (FLEX) approximation, we explore the charge-density wave (CDW) and superconductivity in the layered transition metal dichalcogenides (TMDs). A quantitative analysis on a simplified model of the 2H-TaS<sub>2</sub> is presented. It is demonstrated that the CDW may originate from a combined effect of the scattering between flat bands and an intrinsic property of the off-site Coulomb repulsions. Moreover, the effect of the off-site Coulomb repulsion on the competition of the CDW and superconductivity is elaborated.

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As an early discovered family of materials in which charge-density wave (CDW) and superconductivity (SC) co-exist at low temperatures,<sup>1</sup> the mechanism of CDW in layered transition metal dichalcogenides (TMDs) has not been fully understood yet. Although various theoretical proposals including the Fermi surface nesting,<sup>2</sup> the saddle-point scattering,<sup>3</sup> and the gapless CDW due to the variation in the electron-phonon coupling<sup>4</sup> have been suggested, its origin seems still debatable. As an intriguing feature of the CDW phase in the TMDs, the CDW wave vectors in this family of materials are almost located about  $\mathbf{Q}_i = \mathbf{b}_i/3$ , where  $\mathbf{b}_i$  are the three reciprocal lattice vectors for an inherent triangular lattice of transition metal ions with lattice spacing  $a$  [ $|\mathbf{b}_i| = 4\pi/(\sqrt{3}a)$ ],<sup>5</sup> which suggests likely a common origin of the CDW state in this class of materials. Another issue that has attracted much attention is the competition between CDW and superconductivity in TMDs. By changing the physical properties in a controlled way (intercalation of foreign atoms, changing the pressure, etc.), the possible relationship between the CDW and SC has been studied experimentally.<sup>6-8</sup> After intercalation with sodium atoms, the CDW transition temperature ( $T_{CDW}$ ) was observed to be strongly suppressed, while the superconducting critical temperature ( $T_c$ ) was seen to increase.<sup>6</sup> It was also reported that in TMDs,  $T_c$  increases under pressure while  $T_{CDW}$  decreases.<sup>7,8</sup> In addition, from TaSe<sub>2</sub> through TaS<sub>2</sub> and NbSe<sub>2</sub> to NbS<sub>2</sub>,  $T_c$  increases while  $T_{CDW}$  decreases.<sup>1,9</sup> The observation of the various competition behaviors between the CDW and superconductivity in various materials may imply that this kind of competition is intrinsic to some extent.

In this paper, based on an extended Hubbard model, we propose a scenario to understand the above-mentioned CDW and superconductivity as well as their competition, with a quantitative analysis on the 2H-TaS<sub>2</sub> using the fluctuation exchange (FLEX) approximation. 2H TMDs consists of layers of two-dimensional (2D)-triangular lattices of transition metals with the layers of chalcogen in a hexagonal sandwich arrangement. Similar somewhat to the cases of NaCoO<sub>2</sub>,<sup>10</sup> we assume that Coulomb interactions also play a significant role in the present system. To describe effectively both the

CDW and superconductivity, we consider the following single band extended Hubbard model on the 2D triangular lattice,<sup>11</sup>

$$H = \sum_{ij,\sigma} (t_{ij}c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{ij} V_{ij} n_i n_j - \mu \sum_{i\sigma} n_{i\sigma}, \quad (1)$$

where  $t_{ij}$  denotes the hopping constant,  $U$  the on-site Coulomb repulsion,  $V_{ij}$  the off-site Coulomb repulsion, and  $\mu$  the chemical potential. By fitting the local density approximation (LDA) results for 2H-TaS<sub>2</sub>,<sup>12,13</sup> we may have a simplified tight-binding dispersion

$$\begin{aligned} \epsilon_{\mathbf{k}} = & -2t_1[2 \cos(k_x/2)\cos(\sqrt{3}k_y/2) + \cos(k_x)] \\ & -2t_2[2 \cos(3k_x/2)\cos(\sqrt{3}k_y/2) + \cos(\sqrt{3}k_y)] \\ & -2t_3[2 \cos(k_x)\cos(\sqrt{3}k_y) + \cos(2k_x)] \end{aligned}$$

with  $(t_1, t_2, t_3) = (0.16, -1, -0.068)$  ( $t_2$  is set as the unit hereafter).

Our calculations are based on the fluctuation exchange (FLEX) approximation,<sup>14,15</sup> which is a self-consistent conserving approximation to the 2D Hubbard model. The FLEX method was also extended in principle to study the extended Hubbard model by Esirgen *et al.*,<sup>16,17</sup> while its operation is extremely complicated to be extended to the cases with the high-order neighbors. Without loss of the essential physics, here we adopt a simplified version of the FLEX approximation,<sup>18,19</sup> which is a kind of random-phase approximation (RPA) with dressed Green's functions. Under this scenario, the self-energy is given by

$$\Sigma(k) = \frac{T}{N} \sum_q V_{eff}(k-q)G(q), \quad (2)$$

where

$$V_{eff}(q) = \frac{3}{2}U^2\chi_s(q) + \frac{1}{2}[U + 2V(\mathbf{q})]^2\chi_c(q) - V(\mathbf{q}). \quad (3)$$

Here

$$\begin{aligned}
V(\mathbf{q}) = & 2V_1[2 \cos(q_x/2)\cos(\sqrt{3}q_y/2) + \cos(q_x)] \\
& + 2V_2[2 \cos(3q_x/2)\cos(\sqrt{3}q_y/2) + \cos(\sqrt{3}q_y)] \\
& + 2V_3[2 \cos(q_x)\cos(\sqrt{3}q_y) + \cos(2q_x)]
\end{aligned}$$

with  $V_{1,2,3}$  the nearest-neighbor (NN), the next-NN, and the third-NN Coulomb repulsions, respectively. The spin susceptibility is expressed as

$$\chi_s(q) = \frac{\bar{\chi}_0(q)}{1 - U\bar{\chi}_0(q)}, \quad (4)$$

and the charge susceptibility is written as

$$\chi_c(q) = \frac{\bar{\chi}_0(q)}{1 + [U + 2V(\mathbf{q})]\bar{\chi}_0(q)}, \quad (5)$$

with the irreducible susceptibility,  $\bar{\chi}_0(q) = -T/N\sum_k G(k+q)G(k)$ . The electron Green's function is given by

$$G(k) = [i\omega_n - \epsilon_k - \Sigma(k)]^{-1}. \quad (6)$$

In the above equations,  $k \equiv (\mathbf{k}, i\omega_n)$  and  $q \equiv (\mathbf{q}, i\nu_n)$  are used. These equations were solved self-consistently, where  $64 \times 64$   $\mathbf{k}$  point meshes and up to 2048 Matsubara frequencies  $\omega_n = (2n+1)\pi T$  are taken up. The electron density is determined by the chemical potential  $\mu$  from the equation  $\langle n \rangle = 1 - 2T/N\sum_k G(k)$ . Since the Fermi level fills almost half the lowest of the  $5d$  bands contributed by the transition metal, we here focus on the half-filling case ( $\langle n \rangle = 1$ ).

A system is unstable to the formation of the CDW state with the wave vector  $\mathbf{Q}$  when the charge susceptibility  $\chi_c(\mathbf{Q}, 0)$  diverges. This condition is identical to  $1 + [U + 2V(\mathbf{Q})]\bar{\chi}_0(\mathbf{Q}, 0) = 0$  as inferred from Eq. (5). Given the on-site Coulomb repulsion  $U$  ( $U$  is positive), the satisfaction of the above condition depends on two factors, namely, the irreducible susceptibility  $\bar{\chi}_0(\mathbf{Q}, 0)$  and the off-site Coulomb interaction  $V(\mathbf{Q})$ .

Let us first examine the bare susceptibility calculated from the LDA energy band (the electron-electron interaction is not included),  $\chi_0(\mathbf{q}, 0) = -T/N\sum_{\mathbf{k}} G_0(\mathbf{k} + \mathbf{q}, 0)G_0(\mathbf{k}, 0)$ , which is plotted in Fig. 1(a). One can see that there is a maximum in  $\chi_0(\mathbf{q})$ , which is close to  $\mathbf{q} = \mathbf{b}_i/3$ . Indeed, quite similar structure in  $\chi_0(\mathbf{q}, 0)$  along the  $\Gamma$ - $M$  direction has been obtained for  $1T$ -TaSe<sub>2</sub> and  $1T$ -TaSe<sub>2</sub> from the energy band calculation.<sup>20</sup> So, it is expected that a maximum of  $\chi_0(\mathbf{q}, 0)$  close to  $\mathbf{q} = \mathbf{b}_i/3$  is a common feature of  $2H$  TMDs.

However, one could not expect the emergence of the CDW merely from the bare susceptibility shown in Fig. 1(a), in which no signal of the divergence will occur. We therefore turn to the effect of the off-site Coulomb interaction  $V(\mathbf{q})$ . Intriguingly, the next-NN Coulomb repulsion  $V_{2nd-NN}(\mathbf{q}) = 2V_2[2 \cos(3q_x/2)\cos(\sqrt{3}q_y/2) + \cos(\sqrt{3}q_y)]$  reaches the negative maximum at the wave vector  $\mathbf{q} = \mathbf{b}_i/3$ , which implies that the next-NN Coulomb repulsion enhances the charge susceptibility at the wave vector  $\mathbf{q} = \mathbf{b}_i/3$ , the CDW wave vector of  $2H$  TMDs. Also remarkably,  $V_{NN}(\mathbf{q}) + V_{3rd-NN}(\mathbf{q})$  reaches a local minimum at  $\mathbf{q} = \mathbf{b}_i/3$  with  $V_1 : V_3 = 2 : 1$  (inversely proportional to the ratio between the distance of the NN and the third-NN). As a result, there must

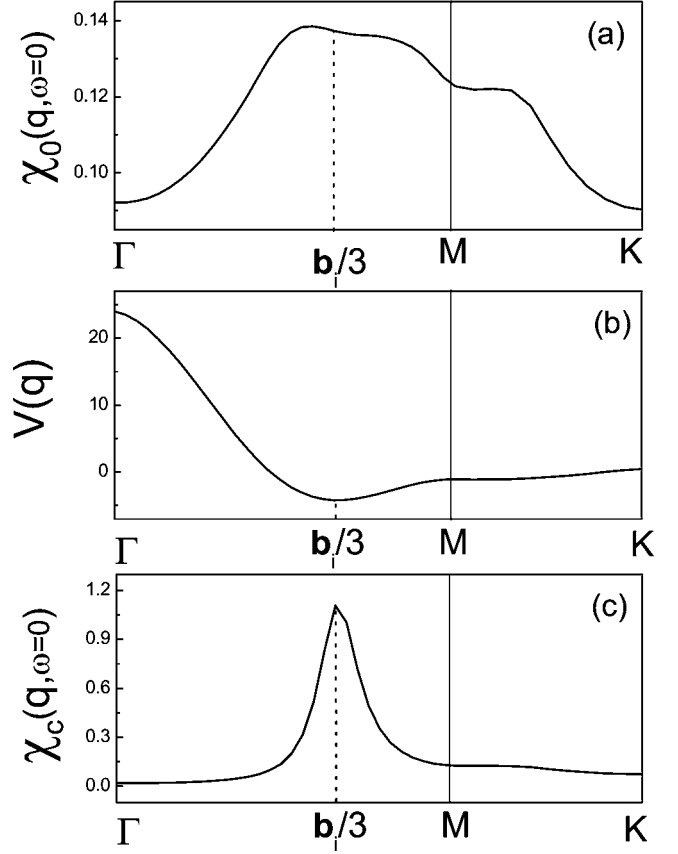


FIG. 1. (a) The bare susceptibility  $\chi_0(\mathbf{q}, 0)$  at  $T=0.3$ . (b)  $V(\mathbf{q})$  with  $(V_1, V_2, V_3) = (1.75, 1.40, 0.875)$ . (c) The charge susceptibility  $\chi_c(\mathbf{q}, 0)$  at  $T=0.3$  for  $U=2.0$  and  $(V_1, V_2, V_3) = (1.75, 1.40, 0.875)$ .

be a minimum for  $V(\mathbf{q}) = V_{NN}(\mathbf{q}) + V_{2nd-NN}(\mathbf{q}) + V_{3rd-NN}(\mathbf{q})$  at  $\mathbf{q} = \mathbf{b}_i/3$  with  $V_1 : V_3 = 2 : 1$  regardless of  $V_2$  amplitude. To ensure the uniqueness of the CDW wave vector without loss of generality, we assume that the off-site Coulomb repulsions are  $(V_1, V_2, V_3) = (1.75, 1.4, 0.875)$ .<sup>21</sup> Under this choice of parameters, we calculate the charge susceptibility by solving the set of self-consistent Eqs. (2)–(6), with a typical result being presented in Fig. 1(c). Obviously, a sharp peak is located at  $\mathbf{q} = \mathbf{b}_i/3$ , which signifies the appearance of a CDW at the wave vector  $\mathbf{b}_i/3$ .

Combining this feature with the maximum structure of  $\chi_0(\mathbf{q})$  around the same wave vector, we note that a minor change of the bare susceptibility  $\chi_0(\mathbf{q})$  induced modification due to the energy band structure would not alter the CDW wave vector. In this sense, we may understand the reason why the CDW wave vector is almost unchanged in  $2H$  TMDs.

A striking consequence of the dominance of the next-NN hopping constant  $t_2$  (Ref. 22) is the appearance of a rather “flat” band around the  $M$  point as seen in Fig. 2(a). At the CDW critical temperature, the scattering between the “flat” bands around the  $M$  points could contribute significantly to the CDW transition because we may always find portions of two flat bands around the  $M$  points which are connected by  $\mathbf{b}_i/3$ , due to the broadness of these flat bands as schematically illustrated in the inset of Fig. 2.

We now note two points about the combined effect on the

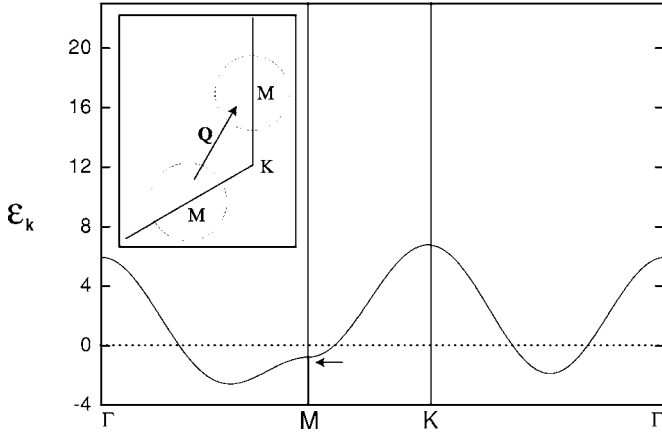


FIG. 2. The tight-binding dispersion by fitting the LDA results. Dotted line denotes the chemical potential  $\mu=0$ . Arrow indicates the flat band near  $M$ . Inset, schematic illustration of the two nearest flat bands around the  $M$  points (enclosed by the dashed line), and the scattering between them may be connected by  $\mathbf{Q}=\mathbf{b}/3$ .

formation of the CDW proposed here. First, the scattering between the flat bands leads only to the enhancement (rather than the divergence) of  $\chi_0(\mathbf{q}, 0)$ , that is, the bare energy band structure is not sufficient to drive the system into the CDW state without the off-site Coulomb interactions. Second, the flat bands which contribute mainly to the formation of the CDW may be around the  $M$  point, rather than in the  $\Gamma$ - $K$  direction as suggested in the saddle point mechanism.<sup>3</sup>

The present scenario based on the extended Hubbard model enables us to investigate the competition between the CDW and superconductivity in  $2H$  TMDs. As we shall see below, the magnitude of the off-site Coulomb interaction may play a role to characterize the competition between the CDW and superconductivity in a natural way, in that the CDW state shows up with a strong off-site repulsion while the superconducting order is favored by a weak off-site repulsion. As mentioned before, the intercalation of sodium ions into  $2H$ -TaS<sub>2</sub> provides a useful way to study the competition between the CDW and superconductivity.<sup>6</sup> In our model, the intercalation of sodium ions is reasonably supposed to introduce a screening effect (and possibly to enlarge the in-plane lattice constants) which reduces the strength of the off-site Coulomb repulsions. For simplicity, we fix the ratios of  $(V_1, V_2, V_3)$  and set them to be  $(1, 0.8, 0.5)V$ . We will change the magnitude of the off-site Coulomb repulsion to study its effect on both the CDW and superconductivity. In principle, Eq. (5) will diverge at the CDW critical temperature  $T_{CDW}$ . But in realistic self-consistent numerical calculations, the divergence cannot occur exactly, because the iteration will end once a divergency approaches. Therefore, to characterize the emergency of the CDW qualitatively, we may define  $T_{CDW}^*$  as the calculated “transition” temperature at which  $\chi_c(\mathbf{q}, 0) = 10\bar{\chi}_0(\mathbf{q}, 0)$ . On the other hand, the superconducting critical temperature  $T_c$  can be calculated by solving the Éliashberg equation,

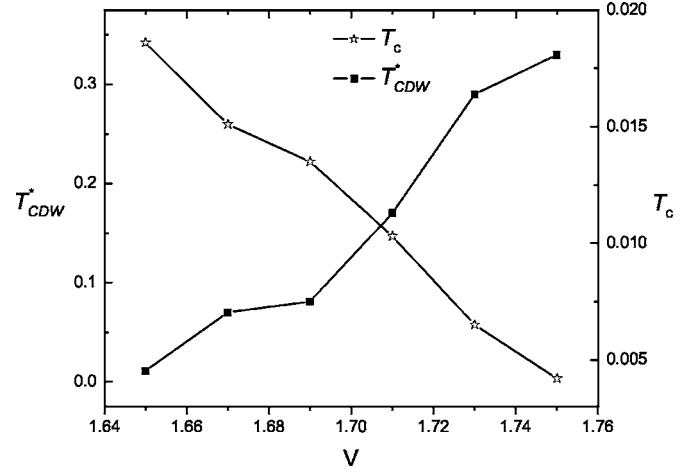


FIG. 3. The superconducting transition temperature  $T_c$  and the calculated ‘transition’ temperature of CDW  $T_{CDW}^*$  (see text) versus the off-site Coulomb interaction for  $U=2.0$  (filled squares,  $T_{CDW}^*$ ; stars,  $T_c$ ).

$$\lambda\varphi(k) = -\frac{T}{N} \sum_q V_{pair}^{s(t)}(k-q) |G(q)|^2 \varphi(q), \quad (7)$$

where the spin-singlet and spin-triplet pairing interactions are

$$V_{pair}^s(q) = \frac{3}{2}U^2\chi_s(q) - \frac{1}{2}[U + 2V(\mathbf{q})]^2\chi_c(q) + U + V(\mathbf{q}), \quad (8)$$

and

$$V_{pair}^t(q) = -\frac{1}{2}U^2\chi_s(q) - \frac{1}{2}[U + 2V(\mathbf{q})]^2\chi_c(q) + V(\mathbf{q}). \quad (9)$$

Once the eigenvalue  $\lambda$  reaches unity, we have  $T=T_c$ .

$T_{CDW}^*$  and  $T_c$  versus the off-site Coulomb repulsion  $V$  are shown in Fig. 3(a) for  $U=2.0$ . The competition between the CDW and superconductivity is clearly seen, noticing that  $T_c$  is enhanced with the decrease of  $V$  while the CDW “transition” temperature  $T_{CDW}^*$  is suppressed significantly. For example, the CDW “transition” temperature and the superconductivity critical temperature are estimated to be  $T_{CDW}^*=0.33$  and  $T_c=0.004$ , respectively, when the off-site Coulomb repulsion is assumed to be  $V=1.75$ . If  $V$  is reduced to 1.65,  $T_{CDW}^*$  will be suppressed to be 0.011 while  $T_c$  is elevated to be 0.019. When we turn off the off-site Coulomb interaction  $V$ , the superconductivity comes from the spin-fluctuation mediated pairing due to the on-site interaction  $U$  as can be seen from Eq. (8). With the increase of  $V$ , the pairing interaction is suppressed by the charge fluctuation which is enhanced [Eqs. (8) and (5)]. This shows that the competition between CDW and superconductivity is due to the competition between spin and charge fluctuations.

To analyze the effect of  $V(\mathbf{q})$  on superconductivity and CDW instability, we present a schematic plot Fig. 4 to illustrate the superconducting pairing potentials  $V_{pair}^s$  and  $V_{pair}^t$  versus the off-site Coulomb repulsion  $V$ , where the irreduc-

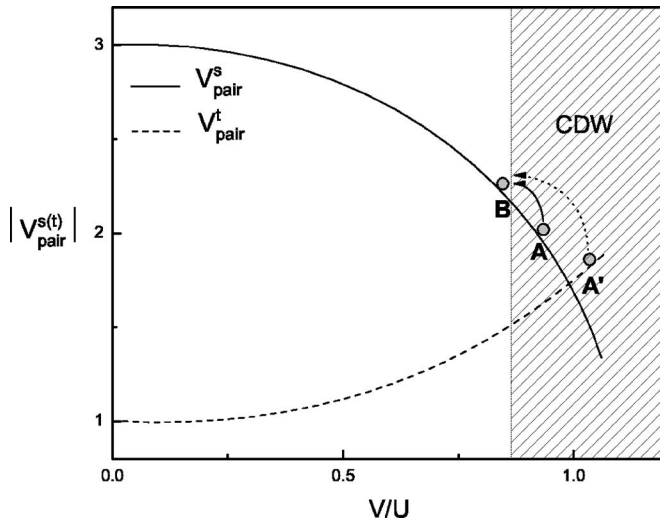


FIG. 4. A schematic diagram for pairing potentials, where  $\bar{\chi}_0(q)$  is assumed to be  $q$  independent for illustration.

ible susceptibility  $\bar{\chi}_0(q)$  is taken to be  $q$  independent for illustration. The shaded region represents the region where a CDW state exists. We can see that the pairing potential in the spin-singlet channel  $V_{pair}^s$  decreases monotonously, while that in the spin-triplet channel  $V_{pair}^t$  increases monotonously. They intersect in the parameter region where a CDW exists (since the superconducting pairing potentials have a close connection to the corresponding  $T_c$ 's, i.e, the larger the  $V_{pair}$ , the higher the  $T_c$ , the favored pairing type of superconducting transition in the channel with a larger pairing potential).

As seen in Fig. 4, from the A point to the B point, the system can change from the CDW region (point A) to the non-CDW region (point B) by reducing the off-site Coulomb repulsion  $V$ , accompanied by an enhancement in the superconducting instability. On the other hand, it is interesting to note that, in a system where the off-site Coulomb repulsion is strong enough, spin-triplet superconductivity may be realized in the CDW region (point A' in Fig. 4). Then, with the decreasing of the off-site Coulomb repulsion the system may transfer from a spin-triplet superconducting state to a spin-singlet superconducting state. This phenomenon should be interesting and we wait for the research in future experiments.

In summary, based on the extended Hubbard model and using the fluctuation exchange (FLEX) approximation, we have explored the charge-density wave and superconductivity as well as their competition in layered transition metal dichalcogenides (TMDs). The intriguing property of the charge-density wave in  $2H$  TMDs is demonstrated as a combined effect of the energy band structure and the intrinsic property of off-site Coulomb repulsions. The effect of the off-site Coulomb repulsion on the competition of the CDW and superconductivity is elaborated.

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<sup>21</sup>An unexpected peak of  $\chi_c(\mathbf{q})$  is also seen at the middle point of  $\Gamma-K$  when  $(V_1:V_2:V_3)=(2:1.16:1)$ . However, this peak is very sensitive to the  $V_2$  amplitude: the peak is suppressed significantly with a slight increase of  $V_2$  amplitude. In this sense, we believe that the CDW is unlikely to occur at that point in the realistic system.

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