Effects of magic angle on crystal and electronic structures of bilayer transition metal dichalcogenides

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Abstract:
In this work, we employ the LDA, GGA and GGA with four vdW corrections to study crystal and electronic structures of bilayer transition metal dichalcogenides (TMDs) with different magic angles (Moiré superlattice). Our results indicate the GGA interlayer distances of bilayer TMDs with magic angles are smaller than that of normal bilayer, which is the opposite of the LDA case. Comparing the experimental and theoretical data, we consider that the pure GGA is suitable for study of Moiré superlattice while vdW correction methods still needs to be further optimized. The GGA results show that magic angle can shorten the interlayer distance and thus narrow the bandgap and widths of valley band and conductivity band. Our study not only supports valuable information for application possibility of TMD Moiré superlattice but also stimulates more related research.
I. Introduction

Since graphene was stripped from graphite, researchers have devoted a great deal of vigor to study two-dimension (2D) materials. Finding new 2D materials and modifying crystal and electronic structures of the existing are two hot spots of current researches. In addition to traditional methods, some new strategies such as strain, electric field, and magic angle are applied to modify 2D materials for obtaining novel physical properties. For example, softening phonon and band edge change such as band gap variation and a transition from direct to indirect band gap were detected in strained transition-metal dichalcogenide (TMD) 2D crystal. Theoretically, it is reported that vertical electric field can induce the change of band gap of bilayer TMDs. Bilayer graphene with small magic angle (namely Moiré superlattice) was predicted to can lead to strong coupling between layers, remarkably flat band and nearly zero of the Fermi velocity.

Theoretical research on TMDs with magic angle is not as extensive and deep as graphene, although TMD Moiré superlattices experimentally show interesting physical and chemical properties. Especially, interlayer distance dependency of magic angle is rarely studied. Previous studies have either used a fixed interlayer distance or a suitable functional to get a result that agrees with the experiment. As known, the interlayer distance has a non-negligible impact on electronic structure of TMDs although van der Waals (vdW) force between layers is weak. Previous report shows that the increase of interlayer distance can enlarge the band gap size of normal bilayer MoS$_2$. Moreover, the influence of the structure optimization strategy on the interlayer distance is often overlooked. Thus, it is necessary and interesting to use different optimization strategies to systematically study effects of magic angle on crystal and electronic structures of bilayer TMDs.

In the following, we choose two representative layered TMDs X$_2$S$_2$ (X= Mo, Cr) as research object. Firstly, we use six correlation exchange functionals and two optimization strategies to obtain the optimized Moiré superlattices with three magic angles. The calculation results show the optimization method of fixed c-axis length and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation potential is suitable for
study on geometric and electronic structures of Moiré superlattice. It is predicted that the magic angle can reduce layer spacing and bandgap for XS₂ (X= Mo, Cr).

II. COMPUTATIONAL METHODS

We use the Vienna Ab Initio Simulation Package (VASP)\textsuperscript{25,26} to perform the first-principles calculations and choose the local density approximation (LDA)\textsuperscript{27} and the generalized gradient approximation (GGA), respectively. For GGA, the Perdew–Burke–Ernzerhof (PBE) exchange correlation functionals\textsuperscript{28} with four van der Waals (vdW) corrections are employed. We severally adopt fully optimization and fixed c-axis length optimization to obtain lowest-energy structures. The cutoff energy, total energy and force criterions and \( k \)-point mesh are set to 500 eV, 10\(^{-5} \) eV, 0.01 eV Å\(^{-1} \) and \( 5 \times 5 \times 1 \) in all optimization calculations. However, we choose denser \( k \)-point mesh of \( 15 \times 15 \times 1 \) for accurate self-consistent calculation (SCF). For band structures calculations, the total number of \( k \)-point along the high-symmetry lines is 110.

III. RESULTS AND DISCUSSIONS

A crystal structure

Firstly, in order to obtain Moiré superlattices of bilayer XS₂ (X= Mo, Cr), one can define commensurate cell vectors \( A (m, n, a_1, a_2) \) and \( B (m, n, a_1, a_2) \)\textsuperscript{29-31}:

\[
A = na_1 + ma_2, \tag{1}
\]

\[
B = -ma_1 + (m + n)a_2, \tag{2}
\]

where \( m \) and \( n \) are integers, and the basis vectors \( a_1 \) and \( a_2 \) with the lattice constants \( a_0 \) of TMDs are defined by:

\[
a_1 = \left( \frac{\sqrt{3}}{2} - \frac{1}{2} \right) a_0, \tag{3}
\]

\[
a_2 = \left( \frac{\sqrt{3}}{2} - \frac{1}{2} \right) a_0. \tag{4}
\]

When one layer rotates by magic angle \( \theta \), the vector \( A \) on this layer coincides with \( B \) vector on the other layer, and then Moiré superlattice is formed. There is such a
relationship between $\theta$ and $(m, n)$:

$$\cos \theta = \frac{m^2 + 4mn + n^2}{2(m^2 + mn + n^2)}.$$  \hspace{1cm} (5)

Thus, the total number of atoms in the in the primitive cell for $XS_2$ ($X = \text{Mo, Cr}$) Moiré superlattice is

$$N = 6(m^2 + mn + n^2).$$  \hspace{1cm} (6)

Considering the limited computing resources, we only study three representative magic angle structures (see Fig. 1) that correspond to $m, n$ and $N$ listed in Table I. It is worth mentioning that a $2 \times 2 \times 1$ supercell containing 24 atomss is adopted for calculations of normal structure with $\theta = 0^\circ$.

Table I Magic angles $\theta$ corresponding to $(m, n)$ and total number $N$ in the primitive cell.

| $(m, n)$ | $\theta$ | $N$ |
|----------|----------|-----|
| (1, 1)   | $0^\circ$ | 6   |
| (2, 3)   | 13.2$^\circ$ | 114 |
| (1, 2)   | 21.8$^\circ$ | 42  |
| (1, 3)   | 32.2$^\circ$ | 78  |

The interlayer distances (ID) is defined by the distance between Mo atomic layers (see Fig. 1(a)). IDs of the bilayer $XS_2$ ($X = \text{Mo, Cr}$), attained by fully optimization strategy (marked by A) and the optimization method of fixed c-axis length (marked by B), are plotted in Fig. 2 and Fig. 3, respectively. For normal structure of bilayer MoS$_2$, the interlayer distance (ID) by A ranges from 6.0255 Å to 7.2334 Å, and that by B ranges from 6.4264 Å to 7.7293 Å. No matter which optimization strategy, the maximal and minimal IDs come from GGA and LDA, respectively. It is quite acceptable since pure GGA and LDA normally overestimates and underestimates lattice constants, respectively. The experimental ID of bilayer MoS$_2$ is 7.0 Å that is smaller than theoretical bulk’s ID 6.14 Å (no experimental data). Obviously, the GGA
ID of bilayer by A strategy best matches the experimental data, although their difference reaches up to 3%. It is perfectly acceptable because current experimental measurement methods still face huge challenges such as the effects of instrument accuracy and substrate on ID. For instance, experimental ID of bilayer graphene is 3.8 Å while its error reaches 1.3 Å[32]. Thus, it is not scientific to judge the accuracy of theoretical method completely from the agreement between theoretical and present inaccurate experimental data. The GGA ID of normal structure by A or B strategy is larger than that of magic angle structures. Conversely, The LDA ID of normal structure by A strategy is smaller than that of the other structure, which is agreement with previous work[16]. However, the LDA IDs by B strategy hardly change with the magic angle. LDA IDs are sensitive to the optimization strategy. These may suggest that the GGA results have more credibility than the LDA results.

Interestingly, in the most cases, the GGA vdW correction leads to the opposite trend to pure GGA: magic angel causes larger ID. The GGA-DFT-D2 ID of zero angle structure by A strategy is smaller ~0.1 Å than that of magic angle structures, although corresponding IDs by B strategy are almost the same and the difference between each other is less than 0.01 Å. For the GGA-vdW-DF, the ID by A of 13.2° is smaller, nevertheless, it by B is larger than that of zero angle structure. The IDs of 21.8° and 32.2° by both A and B strategy are larger than that of zero angle structure. For the GGA-dDsC, the IDs of 13.2°, 21.8° and 32.2° by A strategy are larger about 0.25 Å than that of zero angle. However, their IDs by B strategy are smaller than that of zero angle. The case of GGA-vdW-DF2 is the same as the GGA-dDsC. However, the difference of GGA-vdW-DF IDs of magic angle structures, between by A and B strategies, is not as large as that of GGA-dDsC. These imply GGA-vdW method is dependent of the optimize strategy and thus it is precisely at this point that the feasibility of this method is not high, and GGA-vdW method still needs to be further optimized.

CrS$_2$ as important member of TMDs attract little attention due to the difficult to
synthesize bulk and its 2D counterpart. Inspiringly, the 2H, 1T, and 1T’ structures coexisting were observed in the monolayer CrS$_2$ prepared via the chemical vapor deposition (CVD) method. Thus, it is much possible that bilayer CrS$_2$ with pure 2H structure is grown via CVD. It is necessary and interesting to study geometric and electronic structures of bilayer CrS$_2$ with different magic angles. We find that no matter what optimization strategy is adopted, the GGA IDs of bilayer CrS$_2$ with any magic angles are larger than that of bilayer MoS$_2$, although atomic radius of Cr is smaller than that of Mo. However, the other five types of IDs for bilayer CrS$_2$ are smaller than that of bilayer MoS$_2$. All types of IDs (except for GGA) of bilayer CrS$_2$ with zero angle are larger than that of 13.2°, 21.8° and 32.2°, which is the same with bilayer MoS$_2$ case.

Total energy each atom $E_{atom}$ for all Moiré superlattices of TMDs are showed in Fig. 4 and Fig. 5. The difference of $E_{atom}$ between by A and B strategy are negligible. In the case of the same exchange–correlation functional, the $E_{atom}$ difference between different magic angles structures is also negligible, which can be masked by thermal vibration of atom at ambient temperature. Therefore, from the view of energetics, it is possible to experimentally prepared Moiré superlattices of TMDs. The GGA-vdW-DF and GGA-vdW-DF2 $E_{atom}$ are obviously higher than the other $E_{atom}$. In fact, the comparison between the total energy by different exchange–correlation functional is no point.

B electronic structures

In this section, we put focus on effect of magic angle on electronic structure and more especially on bandgap. Previous work has reported that bulk MoS$_2$ and its 2D counterparts except monolayer are indirect bandgap semiconductors. Valence band maximum (VBM) and conduction band minimum (CBM) locate at $\Gamma$ and K high-symmetry points in reciprocal space, respectively. Moreover, one local VBM is at K point, so the direct bandgap is at K point. Thus, there are two obvious photoluminescence (PL) peaks at of 1.6 eV and 1.8 eV corresponding to the indirect
and direct bandgaps. It is noted that PL spectra detects the optical bandgap that is different from electronic bandgap also known as the fundamental (or transport) bandgap. As known, the difference comes from strongly bound excitons that originates from strong Coulomb interactions between n- and p-type carriers. Theoretically, the optical bandgap can be defined as electronic bandgap minus the exciton binding energy. Therefore, electronic bandgap is usually larger than the optical bandgap.

Electronic GGA bandgaps of 0° bilayer MoS₂ structure by A and by B are 1.58 eV and 1.64 eV that are larger than the other types of bandgaps (showed in Fig. 6). The GGA bandgap by B is larger than the optical bandgap attained by PL, which thus exhibit greater rationality than that by A. The GGA bandgaps of bilayer MoS₂ with magic angles are smaller than that with zero angle. However, the case of the LDA bandgaps is the opposite. This possibly attributes to larger GGA IDs than the LDA IDs. We consider that the large ID can leads to large bandgap, which independent of the choice of exchange correlation functionals. Namely, for the same structure, the bandgaps attained by GGA and by LDA should have little difference. For vdW correction bandgaps, the bandgaps of normal structure by A are smaller than that of magic angles. However, using the B strategy, we obtain the opposite: the bandgaps of 0° structure are larger than of magic angle structures. This again implies the present vdW correction method still needs further improvement. The vdW-DF and vdW-DF2 bandgaps are obviously smaller than the other types of bandgaps, because the two vdW corrections belongs to non-local correlation functional that approximately accounts for dispersion interactions.

As shown in Fig. 7, the corresponding bandgaps of bilayer CrS₂ are smaller, compared with that of bilayer CrS₂. It is understandable that Cr element possess stronger metallic property. The GGA bandgaps of normal bilayer CrS₂ are slightly larger than that with magic angles, although the corresponding GGA IDs are obviously larger than IDs of magic angle structures. This suggests that the GGA bandgaps are not sensitive to ID of bilayer CrS₂. Moreover, in most cases, bandgaps of bilayer CrS₂ structures by A and by B are basically consistent with each other.
Sequentially, we focus on the effects of magic angle on the band structures of TMDs. It can be seen from Fig. 8 and Fig. 9 that the GGA band structures of TMDs with magic angles looks clutter because there are more atoms in primitive cells. The magic angles affect the shapes of VB and CB especially near local VBM at K point. The other types of band structures also show magic angle effects (see Figs. S1 and S2, we only plot the GGA-DFT-D2 band structures). Whether using A or B strategy, the magic angles render both VBs and CBs flat. The shape of VB for bilayer CrS₂ with 13.2° seems to be a line. It is worth mentioning that the decrease of VB or CB width usually leads to larger bandgap. However, magic angles render narrow band width accompanied by smaller bandgaps. This band feature is useful in some applications. For instance, flat band and small bandgap support high Seebeck coefficient and electrical conductivity that is good for realizing thermoelectric high merit of figure.

IV. SUMMARY

In conclusion, we have employed the LDA, pure GGA and GGA with four vdW corrections to explore crystal and electronic structures of TDM Moiré superlattices. Our the first-calculation calculations shows pure GGA is better for describing the effect of magic angle on Moiré superlattices than the other although its results is contradict with the LDA results. The GGA ID and bandgap of Moiré superlattices is smaller than that of normal structure. We find that magic angle can lead to flat VB and CB with smaller bandgap, and consider this band feature is possibly valuable in thermoelectric application.

AUTHOR’S CONTRIBUTION

All authors contributed equally to this work.

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DATA AVAILABILITY
The data that supports the findings of this study are available within the article and its supplementary material.

References:
1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
2. X. D. Xu, W. Yao, D. Xiao, and T. F. Heinz, Nature Physics 10, 343 (2014).
3. F. F. Zhu, W. J. Chen, Y. Xu, C. L. Gao, D. D. Guan, C. H. Liu, D. Qian, S. C. Zhang, and J. F. Jia, Nature Materials 14, 1020 (2015).
4. S. Z. Butler, S. M. Hollen, L. Y. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T. F. Heinz, S. S. Hong, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, and J. E. Goldberger, Acs Nano 7, 2898 (2013).
5. Y. J. Fu, E. F. Liu, H. T. Yuan, P. Z. Tang, B. Lian, G. Xu, J. W. Zeng, Z. Y. Chen, Y. J. Wang, W. Zhou, K. Xu, A. Y. Gao, C. Pan, M. Wang, B. G. Wang, S. C. Zhang, Y. Cui, H. Y. Hwang, and F. Miao, Npj Quantum Materials 2, 52 (2017).
6. E. W. Lee, R. Kim, J. Ahn, and B. J. Yang, Npj Quantum Materials 5 (2020).
7. F. Liu, Y. Zhou, Y. J. Wang, X. Y. Liu, J. Wang, and H. Guo, Npj Quantum Materials 1, 16004 (2016).
8. S. Zhou, C. C. Liu, J. J. Zhao, and Y. G. Yao, Npj Quantum Materials 3, 16 (2018).
9. T. Zhou, J. Y. Zhang, H. Jiang, I. Zutic, and Z. Q. Yang, Npj Quantum Materials 3, 39 (2018).
10. L. N. Du, C. Wang, W. Q. Xiong, S. Zhang, C. X. Xia, Z. M. Wei, J. B. Li, S. Tongay, F. Y. Yang, X. Z. Zhang, X. F. Liu, and Q. Liu, 2d Materials 6, 025014 (2019).
11. Y. F. Wu, A. R. Chew, G. A. Rojas, G. Sini, G. Haugstad, A. Belianinov, S. V. Kalinin, H. Li, C. Risko, J. L. Bredas, A. Salleo, and C. D. Frisbie, Nature Communications 7, 10270 (2016).
12. M. R. Brems and M. Willatzen, New Journal of Physics 21, 093030 (2019).
13. R. M. Zhao, T. X. Wang, M. Y. Zhao, C. X. Xia, Y. P. An, S. Y. Wei, and X. Q. Dai, Applied Surface Science 491, 128 (2019).
14. Z. D. Song, Z. J. Wang, W. J. Shi, G. Li, C. Fang, and B. A. Bernevig, Physical Review Letters 123, 036401 (2019).
G. Tarnopolsky, A. J. Kruchkov, and A. Vishwanath, Physical Review Letters 122, 106405 (2019).
S. X. Huang, X. Ling, L. B. Liang, J. Kong, H. Terrones, V. Meunier, and M. S. Dresselhaus, Nano Letters 14, 5500 (2014).
P. C. Yeh, W. Jin, N. Zaki, J. Kunstmann, D. Chenet, G. Arefe, J. T. Sadowski, J. I. Dadap, P. Sutter, J. Hone, and R. M. Osgood, Nano Letters 16, 953 (2016).
S. Horzum, H. Sahin, S. Cahangirov, P. Cudazzo, A. Rubio, T. Serin, and F. M. Peeters, Physical Review B 87, 125415 (2013).
H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund, S. T. Pantelides, and K. I. Bolotin, Nano Letters 13, 3626 (2013).
A. Ramasubramaniam, D. Naveh, and E. Towe, Physical Review B 84, 205325 (2011).
R. Bistritzer and A. H. MacDonald, Proceedings of the National Academy of Sciences of the United States of America 108, 12233 (2011).
C. H. Jin, E. C. Regan, A. M. Yan, M. I. B. Utama, D. Q. Wang, S. H. Zhao, Y. Qin, S. J. Yang, Z. R. Zheng, S. Y. Shi, K. Watanabe, T. Taniguchi, S. Tongay, A. Zettl, and F. Wang, Nature 567, 76 (2019).
Z. Z. Jiang, W. D. Zhou, A. J. Hong, M. M. Guo, X. F. Luo, and C. L. Yuan, Acs Energy Letters 4, 2830 (2019).
M. H. Naik and M. Jain, Physical Review Letters 121, 266401 (2018).
G. Kresse and J. Furthmüller, Physical Review B 54, 11169 (1996).
G. Kresse and J. Furthmüller, Computational Materials Science 6, 15 (1996).
J. P. Perdew and Y. Wang, Physical Review B 45, 13244 (1992).
J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters 77, 3865 (1996).
G. T. de Laissardiere, D. Mayou, and L. Magaud, Nano Letters 10, 804 (2010).
X. Y. Zhao, L. Y. Li, and M. W. Zhao, Journal of Physics-Condensed Matter 26, 095002 (2014).
J. M. B. L. dos Santos, N. M. R. Peres, and A. H. Castro, Physical Review Letters 99, 256802 (2007).
Z. H. Ni, L. Liu, Y. Y. Wang, Z. Zheng, L. J. Li, T. Yu, and Z. X. Shen, Physical Review B 80, 125404 (2009).
M. R. Habib, S. P. Wang, W. J. Wang, H. Xiao, S. M. Obaidulla, A. Gayen, Y. Khan, H. Z. Chen, and M. S. Xu, Nanoscale 11, 20123 (2019).
T. Cheiwchanchamnangij and W. R. L. Lambrecht, Physical Review B 85, 205302 (2012).
Fig. 1 (Color online) Representation of interlayer distance for bilayer TMD (a), Moiré superlattice with three magic angles 13.2°, 21.8° and 32.2°: (b)-(e).
Fig. 2. (Color online) Interlayer distances of bilayer MoS₂ by A and by B using six exchange correlation functionals GGA (a), LDA (b), GGA-DFT-D2 (c), GGA-vdW-DF (d), GGA-dDsC (e) and GGA-vdW-DF2 (f).
Fig. 3. (Color online) Interlayer distances of bilayer CrS$_2$ by A and by B using six exchange correlation functionals GGA (a), LDA (b), GGA-DFT-D2 (c), GGA-vdW-DF (d), GGA-dDsC (e) and GGA-vdW-DF2 (f).
Fig. 4. (Color online) Total energies each atom of bilayer MoS$_2$ by A and by B using six exchange correlation functionals GGA (a), LDA (b), GGA-DFT-D2 (c), GGA-vdW-DF (d), GGA-dDsC (e) and GGA-vdW-DF2 (f).
Fig. 5 (Color online) Total energies each atom of bilayer CrS$_2$ by A and by B using six exchange correlation functionals GGA (a), LDA (b), GGA-DFT-D2 (c), GGA-vdW-DF (d), GGA-dDsC (e) and GGA-vdW-DF2 (f).
Fig. 6 (Color online) Bandgaps of bilayer MoS$_2$ by A and by B using six exchange correlation functionals GGA (a), LDA (b), GGA-DFT-D2 (c), GGA-vdW-DF (d), GGA-dDsC (e) and GGA-vdW-DF2 (f).
Fig. 7 (Color online) Bandgaps of bilayer CrS$_2$ by A and by B using six exchange correlation functionals GGA (a), LDA (b), GGA-DFT-D2 (c), GGA-vdW-DF (d), GGA-dDsC (e) and GGA-vdW-DF2 (f).
Fig. 8 (Color online) GGA Band structures of bilayer MoS$_2$ with magic angles 0° (top row), 13.2° (the second row), 21.8° (the third row) and 32.2° (bottom row). The left and right columns correspond to band structures of bilayer by A and by B, respectively.
Fig. 9 (Color online) GGA Band structures of bilayer MoS$_2$ with magic angles 0° (top row), 13.2° (the second row), 21.8° (the third row) and 32.2° (bottom row). The left and right columns correspond to band structures of bilayer by A and by B, respectively.