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QUANTUM MATERIALS

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Abstract : 2D vdW quantum systems are stable under ambient conditions, exhibit high crystal quality, and are continuous on a macroscopic scale suitable for many technological functionalities. In layered 2D vdW heterostructure systems, valley (K or K0) and sublattice (A or B) provide tunable binary degrees of freedom to modulate the electronic properties leading to topological surface effects, such as the significant quantum Hall effects. Moreover, the 2D honeycomb layers are prone to form various crystallographic reconstructions, with structural variations as compared to their pristine monolayer system. On the other hand, their distinct electronic properties around the Fermi level and their topological properties are affected due to substrate hybridization effect. Magnetism in these 2D materials as case of metal-free magnetism is now area of particular interest due to small spin-orbit coupling and long spin scattering length. The physics of magnetism in magnetic atom free 2D vdW materials and their respective heterostructures is yet to be revealed in a wide range of systems. The long spin flip length of 2D quantum systems has made them potential candidates for spintronic applications where the spin orbit coupling plays important role for electronic device applications. As 2D layers are held together by vdW force, the realization of respective heterostructures offers a rich platform to study fascinating vdW force-driven properties, like, electronic structure and band structure, magnetic and transport properties, spin-orbit coupling or exchange coupling and topological properties induced by proximity effect and catalytic behaviour. Thus, investigation on electronic structure, topological effects and magnetic behaviour of the 2D quantum systems (both monolayer and heterostructure) is one of the active and emerging current research field.

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1. Two Dimensional van der Waals Quantum Systems

Dimensionality is one of the most defining material parameter. However, reducing the dimensionality of a system is often related with exceptional electronic, topological and magnetic properties because of the reduction of available phase space and reduced screening lead to enhanced quantum effect and increased correlations in the systems. As a result, chemical compounds can exhibit dramatically different properties depending on their arrangement in zero dimension (0D), one dimension (1D), two dimension (2D) or bulk three dimension (3D) structure. Although quasi-0D e.g. cage molecules, quasi-1D e.g. nanotubes and 3D objects are extensively studied, 2D materials are now gaining interest for interesting research among these class of materials. Besides, the condensed matter community extensively investigated the Physics of quasi-2D systems that host the fractional quantum Hall eect before the discovery of stable 2D materials. Atomically thin 2D materials, like graphene and its analogues, such as hexagonal boron nitride (h-BN); phosphorene and its analogues, such as the transition-metal dichalcogenides (TMDCs) are presently attracting the research focus because of their fascinating and unique electronic structure which is modulated by van der Waals (vdW) interaction force (shown in Fig. 1). In general, these 2D structures achieve stable geometry and exhibit high crystal quality under ambient conditions in confined dimension, termed as 2D vdW quantum systems, which are suitable to design respective 2D vdW heterostructures. The vdW heterostructure specializes in various potential properties, such as vdW interaction, strong Coulomb interaction, layer dependence, dielectric screening engineering, work function modulation and phase engineering. These properties help the

vdW heterostructures to be explored in various direction with many applications.

Considering the advances in high performance computing and mathematical algorithms, First-principles methods (to model dense and sparse matter) are paramount not only to the discovery and design of new 2D materials, but also for developing our understanding and control of growth morphology. Despite the reliability and accuracy of quantum chemical (QC) and quantum Monte Carlo (QMC) calculations, density functional theory (DFT) still remains the workhorse for exploring larger and more complex systems with significant atomic relaxations such as the graphene, dichalcogenides and related vdW heterostructure systems. Computationally, the scaling of many existing quantum mechanical methods with respect to the system size hinders their applications to large systems like 2D heterostructures in nanoscale range. Thus, quantum mechanical methods like, DFT and tight-binding (TB) basis are preferred to investigate the electronic structure, topological behaviour and magnetism in these 2D quantum systems with varying degrees of computational demands and transferability and with successive developments approaching chemical accuracy. In this aspect, DFT is fairly accurate First principle based method for electronic structure calculation using pseudopotential wave basis, while TB model is taking full potential wave basis. As a result, both DFT and TB form an ideal and generalized option to analyze various properties of these complicated and realistic 2D systems. However, these modern DFT-based approaches are now mature enough with proper caution. Thus, it is possible to use theory to explore the classes of layered vdW materials, where vdW interactions are intrinsically important, and thereby placing us on the

verge of a new era in computational aided materials research. Besides, these 2D materials can be realized experimentally via epitaxial grow process through deposition technique to correlate with the theoretical simulations for various properties (i.e. structural, electronic, magnetic, thermal, topological, transport, catalytic). In this aspect, theory based simulation and experimental analysis can be corroborated to practically understand these 2D monolayer and heterostructure systems in quantum regime.

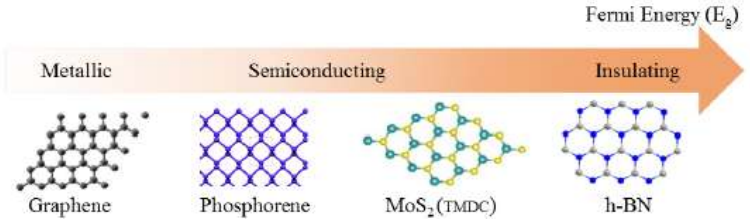

Figure 1
The library of two-dimensional materials, including graphene and its analogues; with an increasing bandgap (in terms of Fermi energy, E_g) from left to right shown in gradient color arrow.

2. Electronic Properties of 2D Quantum Systems

It is obvious that research on graphene has not only rapidly developed in the past decade into a vast research platform that encompasses solid state physics, materials science and engineering, but it has also sparked immense curiosity in a wide range of 2D layered materials with diverse electronic properties. Besides, graphene exhibits unique band structure and exceptionally high carrier mobilities that make it a unique platform for exploring Low Dimensional Physics and for creating a new generation of electronic devices with atomically thin geometry with many drawbacks that have yet to be overcome. In this

aspect, other 2D layer materials introduce more versatility, including conductors, semiconductors with varying bandgaps ranging from 0.5 eV to 3 eV (i.e. phosphorene, MoS_2) and insulators (i.e. h-BN). This broad world of 2D vdW materials with selected finite material properties opens up the possibility of heterostructure assembly at the atomic scale (i.e. quantum regime), creating novel heterostructures that display totally new Physics concepts and enable unique functionalities. In general, the fascinating behaviour of low dimensional systems is more prominent in atomically thin materials and indeed, graphenes unique electronic properties rise from its reduced dimensionality. The quantum mechanical description of the electronic band structure can be simplied by introducing quasi-relativistic particles near the corners of the Brillouin zone, as shown in Fig. 2(a). Therefore, graphene quasiparticles move like electrons that have lost their mass, except that the speed of light is replaced by graphene Fermi velocity, which is some three hundred times smaller. This nature gives rise to many interesting features for graphene electronics and its integration for vdW heterostructure. Besides, the two carbon atoms in the graphene unit cell are replaced by boron and nitrogen atom, respectively which breaks the inversion symmetry in h-BN (shown in Fig. 2(b)). As a result, a large energy gap opens at the valleys, making h-BN an extremely good dielectric and insulator with wide bandgap. Similarly, the electronic structure of MoS_2 consists of one layer of a transition metal molybdenum (Mo) sandwiched between two layers of sulfur with a thickness of 2-3 Å. It has no inversion symmetry, thus retains a finite nonzero bandgap. However, the electronic band structure is complicated due to the strong spin orbit coupling (SoC) interaction, which arises from the high orbital velocities of partially filled

d subshells in the relatively heavy Mo atom (shown in Fig. 2(c)). Considering the case of phosphorene, a layered allotrope of elemental phosphorus, has some interesting properties that arise from its inherent in-plane structural anisotropy (shown in Fig. 2(c)) due to the form of puckered geometry. Consequently, it has an anisotropic electronic band structure, and its charge carriers have anisotropic effective mass. The existing anisotropy has a strong coupling with the lattice strain leading to suitable application of the system as low-dimensional piezoelectricity.

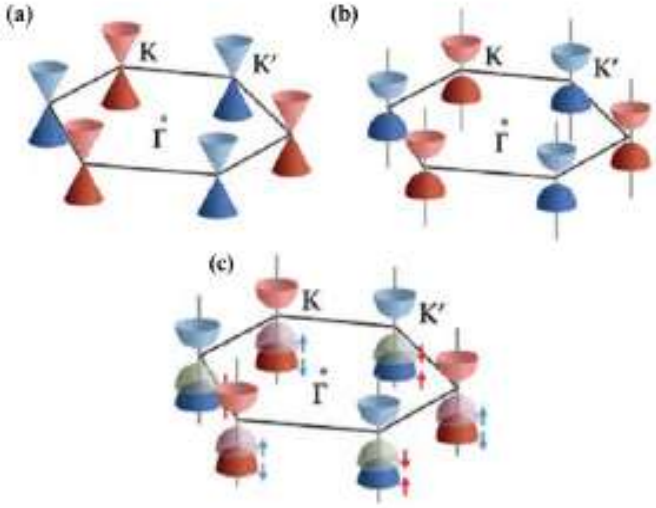

Figure 2

Schematic representation of electronic band structures at the corners of the first Brillouin zone for (a) graphene sheet (conductor), (b) h-BN (insulator with wide band gap) and (c) semiconductor (MoS_2 and phosphorene) with finite band gap.

3. Topological Behaviour of 2D Quantum Systems

In 2D vdW systems, topological ordering is analogous to a conventional 2D electron gas subject to a strong external magnetic field causing electronic excitation gap at the boundaries or surfaces. By definition, topological insulator (TI) is a material that has a nontrivial

symmetry-protected topological order resulting in metallic surface states having Dirac-like spectrum (shown in Fig. 3). In this phase, the electronic band structure is typical to that of an insulator with the Fermi level in between the valence and conduction band. Furthermore, Spin-orbit interaction plays significant role in tuning this behaviour. A specific topological invariant (Z2) is used to distinct between 2D and 3D topological insulators, which defines the ground state of the system. The spin must be either parallel or antiparallel to the particle momentum in real relativistic spin-1/2 fermions. In this line, quasiparticles (at K or K' valleys) in graphene have an analogous pseudo-spin degree of freedom, which describes the wave function symmetry on the two triangular sublattice of graphene hexagonal lattice. From that chiral nature of charge carriers in the system, various electronic properties emerge leading to topological phases and its transformation, such as a half-integer shift in the quantum Hall effect or Klein tunnelling. As a result, non-trivial topological Berry phase is detected first experimentally in graphene, which supplies an important connection to the later discovery of topological insulators. Similar, topological phases can be expected in h-BN system due to its wide electronic bandgap and inversion symmetry, like graphene sheet. The SoC interaction factor splits the valence bands of MoS_2 into two spin polarized bands (i.e. twice the number of spinor). Here, time-reversal symmetry (TRS) requires the spin and momentum degrees of freedom to be coupled with each other such that the K and K' valleys carry opposite spin polarizations. That unique spin and valley texture causes electrons to experience a pseudomagnetic field, which gives rise to distinct topological trivial phases (i.e. so-called valley Hall effect) without applying any external field. Furthermore, both electron

spin and momentum valley of the electrons in the system can be controlled by applying circularly polarized light to tune its property as per potential functionality in the field of spintronics application. Similar, topological behaviour can be logically explained in the anisotropic phosphorene system due to its _finite nonzero electronic bandgap in semiconducting range and TRS, like MoS_2 sheet. Moreover, quantum confinement and the lack of bulk dielectric screening have profound effect on the optical phonon properties of semiconducting phosphorene. Here, the phosphorene monolayer undergoes a transition to a direct electronic bandgap leading to relatively stronger optical phonon absorption and more efficient radiative recombination. This nature provides interesting feedback to consider the novel electron-phonon interaction and respective phonon population distribution in monolayer system.

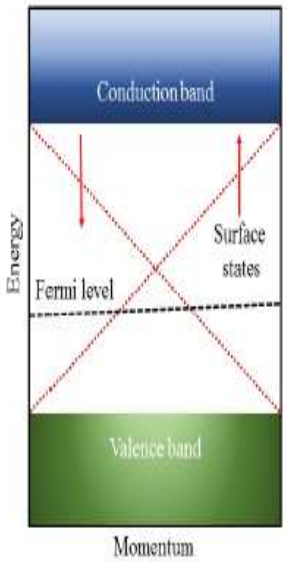

Figure 3
Schematic illustration to show the electronic band structure of a topological insulator in energy vs momentum space.

4. Magnetic Properties of the metal free 2D Systems

Understanding the fundamental difference between vdW 2D and 3D magnetism is informative to understand the driving force of quantum mechanical origin (i.e. exchange interaction) underlying in the ordering of electron spin magnetic moments in an antiferromagnetic system. In this aspect, the mean-field approach of 3D systems does not validate for the length scale of 2D vdW systems, in which the dimensionality (i.e. confinement) effect comes into play. Magnon (i.e., quanta of spin wave) dispersion in such 2D vdW systems attains reduced value compared to that of the 3D counterparts, corresponding to an abrupt onset of magnon density of states (DOS) in 2D vdW systems. For 2D vdW systems without magnetic anisotropy, the spin wave excitation gap reduces. In these materials, any finite nonzero temperatures cause massive magnon excitations and collapsing of the spin order together with the diverging Bose-Einstein statistics of magnons at zero energy. However, a magnon excitation gap opens up and resists the thermal agitations for 2D systems with a uniaxial magnetic anisotropy. In this line, several attempts are performed to create ferromagnetism in nonmagnetic 2D vdW materials since the rise of graphene. One of the mainstream strategies is through introducing vacancies or adding adatoms (i.e. hydrogen and fluorine). Such defect engineering produces local magnetic moments from unpaired electrons, which could be further correlated through conduction electrons in graphene (i.e. itinerant p-magnetism). However, attempts to order these moments in a long-range pattern poses overwhelming challenges in development of the material. Flat band ferromagnetism has been proposed to be realized via extended defects, like zigzag edges of

graphene nanoribbons or grain boundaries of 2D materials. Such defects cause less-dispersed electronic bands that satisfy the huge DOS in a narrow energy scope, leading to the Stoner instability toward a ferromagnetic phase. Remembering the magnetism in 2D vdW systems, the first two reported 2D magnetic atomic crystals are chromium compounds, such as $Cr_2Ge_2Te_6$ (a 2D Heisenberg ferromagnet with small magnetic anisotropy) and CrI_3 (a 2D Ising A-type anti-ferromagnet). Similarly, the magnetic behaviour can be tuned based on the crystal lattice of the 2D vdW systems. However, it is possible to make magnetically ordered chains with finite length and width, so that the finite size ferromagnets behave as spin blocks of super paramagnets with reasonably long spin flipping time, which can provide a practical path toward nanoscale spintronic devices.

5. Two Dimensional van der Waals Heterostructures

In general, these 2D vdW layered materials are usually characterized by extended crystalline planar structures held together by strong in-plane covalent bonds and weak out-of-plane vdW forces. These dangling-bond-free atomic sheets often show extraordinary electronic, topological and magnetic properties in contrast to specific nanostructures that are plagued by dangling bonds and trap states at the surface. These, vdW interactions allow considerable freedom in integrating these 2D layered materials with various nanoscale materials by breaking the vdW bonds to create divers vdW heterostructures without affecting the crystal lattice matching. However, these 2D crystals can be assembled into heterostructures in various methods, like layer-by-layer and interfacial

method. Nevertheless, a large variety of novel prototypes and experiments are going on with these vdW heterostructures, which clearly indicate that these materials are versatile and practical tools for near future experiments and applications.

6. Electronic Properties of vdW heterostructures

In a generalized way, these 2D vdW materials offer great flexibility in terms of tuning their electronic properties. Thus, electronic band-gap engineering can be carried out by changing the number of 2D layers in a given material. However, the rise of vdW materials promotes the possibility of new types of quantum heterostructures with atomically sharp interfaces between the layers of dissimilar 2D vdW materials. Stacking of two or more atomic layers of different vdW materials leads to the rich variety of 2D vdW quantum systems and allows researchers to explore novel and collective electronic, topological and magnetic phenomena at the interfaces. The correlation between electron and spin, phonons, and other electrons can be significantly modulated affecting the charge transport, entropy and total energy in the quantum limit. Moreover, quantum fluctuations are often enhanced and compete with long-range order due to the limited phase-space volume of the heterostructure. As a result, these heterostructures may display emergent electronic phenomena. In other way, the twisting angle between two 2D layers, is an additional degree of freedom in assembling vdW heterostructures. Thus, adjusting the angle between two atomic lattices can result in structures with different electronic properties (i.e. periodic or commensurate structure and incommensurate or quasi-periodic moire

patterns). The important fact is that the physical (i.e. electronic, topological optical and magnetic) properties of such vdW heterostructures often sensitively depend on the interfacial commensurability, thus tuning the twisting angle supports to engineer a large number of combinations of vdW materials. Among the tools for electronic band-structure engineering in vdW heterostruces are the relative alignment between the neighbouring crystals, surface reconstruction, charge transfer, and proximity effects (when one material can borrow the property of another by contact via quantum tunneling or by Coulomb interactions). Thus, the moire structure for graphene on h-BN leads to the formation of secondary Dirac points, commensurate-incommensurate transition in the same system leads to surface reconstruction and gap opening in the electron spectrum, and spin-orbit interaction can be enhanced in graphene by neighbouring TMDC materials.

7. Topological Behaviour and Phase transition in vdW heterosystem

Even more interesting is the specific 2D physics observed in such materials, like, Kosterlitz-Thouless (KT) phase transition in quantum regime, characterized by the emergence of topological order, resulting from the pairing of vortices and antivortices below a critical temperature. Crystals with transition metals in their chemical composition are particularly prone to many-body instabilities such as spin density waves (SDWs), superconductivity and charge density waves (CDWs). Such effects can also be induced by proximity if such 2D vdW crystals are sandwiched with different 2D vdW layer materials. Furthermore, these 2D vdW systems play a specific role in the physics of topological phase

transitions. This transition can be denoted by a topological invariant (Z2) and various phases are detected based on the value of the invariant, like Z2=0 shows trivial phase and Z2=1 shows nontrivial topological phases (i.e. quantum spin hall (QSH) phase). However, it is very rare for a system to have existing long-range order at any finite temperature with a continuous order parameter, implying that even minute thermal fluctuations can destroy order. It is very unique and special that long-range order is possible in 2D vdW systems only at strictly zero temperature (i.e. T=0K). Thus, one can create disorderness in 2D systems by applying an external parameter, like pressure or electric field. In this case, the point at which this 2D system becomes ordered at T=0K is called the quantum critical point, and the transitions are called quantum phase transitions. Thus, it is not the thermal motion that drives the system from order to disorder, but quantum fluctuations in this 2D vdW systems, leading to specific topological phase transitions.

8. Potential Functionalities and outlook of the 2D vdW quantum Systems

The availability of an increasingly broad library of 2D vdW materials with variable electronic properties and the unique ability to integrate into vdW heterostructures enables a new platform for material engineering and device design. The danglingbond-free surface ensures excellent electronic properties and the vdW interlayer interaction allows for considerable flexibility in the systems. The atomically sharp interfaces and highly distinct electronic functions offers a new material prospects and a rich playground for fundamental studies that probe the generation, confinement and transport of charges, exciton, photons and phonons at the limit of single-atom thickness. This empowers the design of a new generation of electronic, energy storage device, catalyst and

spintronics devices with extraordinary performance and unique functionality. Despite the extraordinary potential and considerable progress so far, the challenge of turning these proof of-concept designs into practical technologies should not be understated. Efforts have increased in developing new strategies in understanding the theory and practical implementation of the systems, but current progress is still far from sufficient. The interplay of dimensionality, correlation, charge, orbital character, and topology makes 2D vdW magnetic materials and heterostructures extremely fertile condensed matter systems with a large reservoir of exotic properties. Moreover, another challenge is towards integrating complex 2D vdW heterostructures into functional devices, where a complete understanding of the functional mechanism of these devices is yet to be fully developed. Nonetheless, these new designer materials and unique device structures offer unprecedented opportunities for new applications that represent the future of advance energy storage, catalytic industry, electronics, spintronics and valleytronics.

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