Valleytronics *
A New Way to Communicate With Electrons

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The electronic band structure in crystalline semiconductors represents a relationship between crystal momentum and energy of the electrons and is often depicted by a series of extremum known as valleys. While the use of charge or spin degree of freedom for carrying information is prevalent in today’s technology, the use of electron’s valley degrees of freedom for encoding and processing information (valleytronics) has remained inaccessible for many decades because of inadequate coupling between external excitation and the valley. The advent of two-dimensional materials such as graphene and transition metal dichalcogenides has opened a new avenue for valleytronics which seeks to use valley degrees of freedom to carry and process information, analogues to spin-based spintronics and charge-based electronics. These materials have unique spin-valley locking, imparting a great ability to control and harness electronic valley degrees of freedom with light, electric, and magnetic fields. Here, we present a viewpoint on the fundamental aspects of valleytronics, emphasising valley contrasting characters of two-dimensional semiconductors.

Introduction

In solid-state crystalline materials, the electronic band structures comprise local maxima in the valence band and local minima in the conduction band. These extrema in the valence or conduction band, called ‘valleys’, are determined by the relationship between an electron’s crystal momentum and energy ($\varepsilon - \kappa$ dis-
The electrons and holes occupy these valleys as these are stable points in the band structure and act as low-energy sites for carriers in crystal momentum space (K-space). Therefore, like charge and spin, the electron can be described by the valley degrees of freedom (valley index or valley pseudospin), which specifies its position in the K-space. Due to crystal symmetry, certain K-valleys in $\varepsilon - \kappa$ dispersion are energetically degenerate. If certain distinguishing properties exist for such valleys, it is possible to use valley degrees of freedom for electrons to carry and store information. Valleytronics is conceptually a branch of electronics where the principal aim is to manipulate the valley or momentum degrees of freedom of electrons in a solid state [1]. Recently, there has been considerable interest in the field of valleytronics. The motivation behind this field is to find new systems where valley degrees of freedom can encode and process the information and have an advantage over charge-based electronics and spin-based spintronics. The devices for information storage and processing based on pure valley current are expected to offer low energy operation due to the absence of ohmic heating associated with charge current. Moreover, valleytronics may have an edge over spintronics as the devices can operate in the absence of a magnetic field which primarily introduces stability issues in spin-based electronic devices. Here, we briefly present the basic underlying concepts and related physics associated with valleytronics in 2D semiconducting transition metal dichalcogenides (TMDs).

The ideal valleytronics materials must have two or more degenerate (same energy), and inequivalent valley (different K) states so that one can selectively populate one valley than another. This creates valley polarization and subsequently generates valley current. The early works date back to the 1970s, involving materials such as silicon (Si) and aluminium arsenide (AlAs) with two degenerate valleys. However, due to the lack of strong coupling between external excitation and valley index, it was difficult to precisely control valley degrees of freedom in these materials.
Berry Phase, Spin and Valley Index

After the discovery of graphene, a one-atom-thick 2D layer of carbon atoms, and subsequently 2D semiconducting TMDs such as molybdenum disulphide (MoS$_2$), tungsten disulphide (WS$_2$), etc., the potentials of valleytronics research is on high demand. Because of the broken inversion symmetry coupled with time-reversal symmetry, monolayer MoS$_2$ possess valleys at the inequivalent K (or +K) and K’ (or -K) points in the Brillouin zone (Figure 1). The K (or +K) and K’ (or -K) points in hexagonal 2D materials are time-reversed images of one another, so in general, physical quantities that have odd parity under time reversal are good candidates to distinguish valley states. One of the important physical quantities different for these two inequivalent points is the Berry curvature $\Omega(k)$, where $k$ is the crystal momentum. Berry curvature describes the geometric properties of the electronic bands and is central to understanding band topology-related effects [2].

The electrons in crystalline solids occupy certain states in energy bands called the Bloch states. Bloch states are eigenstates of the translational symmetry operator of the crystal. These states satisfy the periodicity of the underlying crystal potential. Since the translational operator and Hamiltonian commute with each other, they will have simultaneous eigenstates. Quantum mechanically, the electron moves as a wave through a periodic potential in a crystalline solid. An electron in a Bloch state is characterized by its wavevector $k$ (or crystal momentum). So, its velocity moving through the periodic structure is a function of $k$. Considering the electrons to move as wavepackets in $n^{th}$ energy band and using Planck’s relation $\omega_n(k) = \epsilon_n(k)/\hbar$, we obtain the velocity of the Bloch electron as:

$$v = v_n(k) = \nabla_k \omega_n(k) = 1/\hbar \nabla_k \epsilon_n(k),$$  \hspace{1cm} (1)

where $v_n(k)$ is the group velocity and the wave vector $k$ is the quantum number which describes a Bloch state. The dynamics of the Bloch electron in $n^{th}$ energy band, under the uniform electric
field $\mathbf{E}$ is given by the equation of motion:

$$\dot{\mathbf{k}} = \frac{d\mathbf{k}}{dt} = \frac{1}{h} \frac{d\mathbf{p}}{dt} = \frac{q\mathbf{E}}{h} = -\frac{e\mathbf{E}}{h}. \quad (2)$$

Note that under a uniform electric field $\mathbf{E}$, the potential $\phi(r)$ varies linearly in space. As a result, the Hamiltonian of the system no longer commutes with the momentum and breaks the translational symmetry of the crystal. Therefore, Bloch’s theorem cannot be applied. In order to overcome this difficulty, one can choose time-dependent vector potential ($A(t)$) as a gauge for the electric field. Thus, $\mathbf{E} = -\frac{\partial A(t)}{\partial t}$ and $A(t) = -Et$. Therefore, the one-electron Hamiltonian (perturbed) of the crystal in the presence of this electric field $\mathbf{E}$ is given as:

$$\mathbf{H}(\mathbf{r}) = \frac{(\mathbf{p} - qA)^2}{2m} + V(\mathbf{r}), \quad (3)$$

where $q = -e$, $A$ is the vector potential and $V(r)$ is the periodic potential of the lattice. Since the Hamiltonian in (3) has an explicit time dependence, the energy in the system is not conserved. Further, under time reversal symmetry operation ($\hat{T}$), we have $\hat{T} \mathbf{H} \hat{T}^{-1} \neq \mathbf{H}$, implying time reversal symmetry is broken.

According to Bloch’s theorem, the one-particle eigenstates in a periodic potential can be written as $\psi_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot \mathbf{r}}u_{nk}(\mathbf{r})$, where $n$ is the band index, $\mathbf{k}$ is the wavevector of the electron, $u_{nk}(\mathbf{r})$ is a periodic function of lattice and the corresponding Schrödinger equation is $\mathbf{H}\psi_{nk}(\mathbf{r}) = \varepsilon_{nk}e^{i\mathbf{k}\cdot \mathbf{r}}u_{nk}(\mathbf{r})$. Let us denote the one-electron unperturbed Hamiltonian of the crystal and the corresponding Schrödinger equation as:

$$\mathbf{H}_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \text{ and } \mathbf{H}_0\psi_{nk_0}(\mathbf{r}) = \varepsilon_{nk_0}\psi_{nk_0}, \quad (4)$$

where $\mathbf{k}_0$ is the wavevector of the electron in the absence of applied electric field. Then we can write,

$$\mathbf{H}_0e^{i\mathbf{k}_0\cdot \mathbf{r}}u_{nk_0}(\mathbf{r}) = \varepsilon_{nk_0}e^{i\mathbf{k}_0\cdot \mathbf{r}}u_{nk_0}(\mathbf{r}), \quad (5)$$

$$e^{-i\mathbf{k}_0\cdot \mathbf{r}}\mathbf{H}_0e^{i\mathbf{k}_0\cdot \mathbf{r}}u_{nk_0}(\mathbf{r}) = \varepsilon_{nk_0}u_{nk_0}(\mathbf{r}), \quad (6)$$
and
\[ \overline{H_{k_0}u_{nk_0}(r)} = \varepsilon_{nk_0}u_{nk_0}(r) \]
where
\[ \overline{H_{k_0}} = e^{-i\mathbf{k_0}\cdot\mathbf{r}}H_0(\mathbf{r})e^{i\mathbf{k_0}\cdot\mathbf{r}} = \frac{1}{2m}(\mathbf{p} + \hbar\mathbf{k_0})^2 + V(\mathbf{r}). \]  

(7)

Hence, under an electric field, the time-dependent Hamiltonian of the electron with wavevector \( \mathbf{k} \) can be written as:
\[ \overline{H_k(t)} = e^{-i\mathbf{k}\cdot\mathbf{r}}H(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{2m}(\mathbf{p} + \hbar\mathbf{k})^2 + V(\mathbf{r}), \]

(8)

where \( \mathbf{k}(t) = \mathbf{k_0} - \frac{eE_t}{\hbar} \).

Since the Hamiltonian is a slowly varying function of time, the adiabatic theorem in quantum mechanics enables the system to remain in its time-dependent ground state, i.e., if the system starts with initial state \( |\phi_n(0)\rangle = |n(0)\rangle \) and the time evolution of the state is governed by
\[ i\hbar \frac{d}{dt} |\psi(0)\rangle = \overline{H(t)}|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle. \]

(9)

When Hamiltonian is independent of time, \( |n(t)\rangle = e^{-\frac{i}{\hbar}E_n|n(0)\rangle} \).

However, when it is a slowly varying function of time, we can have \( |\psi_n(t)\rangle = c_n(t)|n(t)\rangle \). Plugging this \( |\psi_n(t)\rangle \) in the time-dependent Schrödinger equation above (9), we have
\[ i\hbar c_n(t)|n(t)\rangle + c_n(t)\frac{d}{dt}|n(t)\rangle = E_n(t)c_n(t)|n(t)\rangle. \]

(10)

Applying \( \langle n(t) | \) to both sides of the above equation and integrating thereafter, we can get
\[ c_n(t) = e^{-\frac{i}{\hbar} \int_0^t E_n(t')dt'} e^{-\int_0^t \langle n(t')|n(t') \rangle dt'}. \]

(11)

Further, by adding 1st order correction to the eigenstate, it can be shown that [2]
\[ |\psi_n(t)\rangle = c_n(t)\left(|n(t)\rangle - i\hbar \sum_{n'\neq n} \frac{\delta}{\delta t} \langle n(t)|n(t') \rangle \left| n(t') \right\rangle \right). \]

(12)
where $E_{n'}$ is the energy corresponding to the energy level $n'$. Therefore, using perturbation theory and keeping up to first-order correction to $u_{nk}(r)$, the velocity of the electron in the Bloch state is calculated as:

$$v_n(k) = \langle u_{nk} | \frac{\partial \mathbf{H}}{\partial k} | u_{nk} \rangle = \langle u_{nk} | \frac{1}{m} (\mathbf{p} + \hbar \mathbf{k}) | u_{nk} \rangle.$$

where,

$$|u_{nk}| = |u_{nk}| - i\hbar \sum_{n \neq n'} \frac{|u_{n'k}| \langle u_{n'k} | \frac{\partial}{\partial t} | u_{nk} \rangle}{\epsilon_{nk} - \epsilon_{n'k}}.$$

The velocity can be further reduced to

$$v_n(k) = \frac{1}{\hbar} \frac{\partial \epsilon_{nk}}{\partial k} - i \left( \langle \frac{\partial u_{nk}}{\partial k} | \frac{\partial u_{nk}}{\partial t} \rangle - \langle \frac{\partial u_{nk}}{\partial t} | \frac{\partial u_{nk}}{\partial k} \rangle \right).$$

The Berry connection for band-$n$ is

$$A_n(k) = \langle u_{nk} | \frac{\partial}{\partial k} | u_{nk} \rangle,$$

$$\Omega_n(k) = \nabla_k \times A_n(k) = i \left( \frac{\partial u_{nk}}{\partial k} \times \frac{\partial u_{nk}}{\partial t} \right),$$

therefore,

$$v_n(k) = \frac{1}{\hbar} \frac{\partial \epsilon_{nk}}{\partial k} - \mathbf{k} \times \Omega_n(k).$$

$$\hbar v_n(k) = \frac{\partial \epsilon_{nk}}{\partial k} - \mathbf{E} \times \Omega_n(k).$$

This tells that Berry curvature of the Bloch band is also required for a complete description of electron dynamics. So, in addition to normal group velocity, the electrons also have an anomalous velocity associated with the Berry curvature. Therefore, it is an effective magnetic field that results from the structure of the Bloch bands and is a pseudovector causing the electrons to deflect and result in transverse current and Hall conductance. It’s odd under time-reversal [$\Omega(k) = -\Omega(-k)$] and even under inversion [$\Omega(k) = \Omega(-k)$]. The system with simultaneous space inversion and time reversal symmetry results in zero Berry curvature. So, valley contrasting phenomena can be observed in 2D monolayers with broken inversion symmetry. Therefore, the electrons at
+K and -K valleys will deflect in the opposite direction under the action of the in-plane electric field, which is the so-called valley Hall effect.

Similarly, another physical quantity inequivalent at K and K’ is orbital angular momentum [1, 3]. This quantity is a pseudovector and, therefore, non-equivalent. As absorption and emission of a photon in a material are determined by the initial and final angular momentum states of the electron/hole, the orbital angular momentum states in TMDs play a vital role in determining valley-dependent optical chirality. Moreover, the orbital angular momentum leads to a valley contrasting Zeeman shift under a magnetic field. Since one of the applications of valleytronics is information storage, realizing valley polarization is a prerequisite. Like orbital angular momentum, electrons in TMDs also show valley contrasting spin angular momentum. Spin up and spin down are also a time-reversal picture of each other. The strong spin-orbit coupling in TMDs due to the high Z (atomic number) of transition metals exhibits significant valley spin splitting. The +K and -K valleys show the same spin-splitting value but opposite signs, which are protected by the time-reversal symmetry. This leads to robust coupled spin and valley physics, which could suppress valley relaxations due to spin-flip. The valley-contrasting spin splitting hinders the spin-flip and favours the valley polarization. As a result of this, these materials exhibit strong valley-selective interactions with light, electric and magnetic fields.

Control of Valleys

There has been a continuous exploration of the manipulation of valleys—optically, electrically, and magnetically—in monolayers of TMDs. As mentioned earlier, due to time-reversal symmetry, the electrons have opposite spins in K (or +K) and K’ (or -K) valleys [3–6]. Therefore, one can observe spin-valley locking, which results in valley-dependent optical selection rules. Optical manipulation of valleys generated early breakthroughs in monolayer TMDs as it has a direct bandgap at K (or +K) and K’ (or
The valley optical selection rule also enables the generation and detection of valley coherence. Additionally, these materials possess robust excitons with a binding energy of at least of few hundred (≈500) meV at room temperature. This large binding energy arises due to reduced dielectric screening of Coulomb interaction in 2D materials and is in contrast to III-V semiconductors, which have exciton binding energies of the order of 5–10 meV.

This offers an adequate opportunity to manipulate valley pseudospin optically. Heinz et al. first demonstrated the selective excitation of carriers and subsequent exciton valley polarization optically in monolayer MoS$_2$ using polarization-resolved photoluminescence (PL) spectroscopy [3]. In this experiment, the polarization of the emitted photoluminescence from MoS$_2$ was controlled by selectively exciting carriers into K (or +K) and K' (or −K) via right circularly polarized and left circularly polarized light, respectively (Figure 1). They observed that the emitted light has same polarization as the incident light. The valley optical selection rule also enables the generation and detection of valley coherence. A linearly polarized photon is a coherent superposition of a left and right circularly polarized photon. It can thus transfer optical coherence into excitonic valley coherence (Figure 2a).
Linearly polarized PL from neutral excitons is observed in monolayer WSe$_2$, with a polarization angle that always coincides with the linearly polarized excitation [6].

Similarly, Zhang et al. first manipulated the valleys in an electric double-layer transistor structure with WSe$_2$ thin flakes with 0.6–2.6 nm thicknesses as the channel material [7]. The polarization of electroluminescence (EL) emitted from the device was switched between left and right circular polarization. This was controlled electrically by reversing the polarity of the applied field and the injected charge. The valley contrasting magnetic response has also been observed in TMDCs. The degeneracies of +K and -K valleys are lifted by applying out of plane magnetic field (Figure 2b) due to the valley contrasting orbital magnetic moment. It has been observed that Mo and W based TMDCs have opposite spin splitting in the conduction band. However, small valley magnetic response in these material limits their applicability in valleytronics via magnetic control [1].

**Figure 2.** A schematic representation that shows (a) valley coherence via optical excitations in monolayer TMDs via linearly polarized light and (b) valley manipulation via magnetic control showing valley contrasting Zeeman shift under applied magnetic field $H$. 
Conclusion

In conclusion, even though 2D materials like TMDCs have proved their potential candidature for future valleytronics, harnessing these observed phenomena into viable technology is still in its infancy. The field of valleytronics is rapidly growing with the synthesis of high-quality 2D materials. So far, light has played an important role in materializing the concept of valley polarization as compared to magnetic and electric control. In future, the long-lived dark excitons [9] created at different valley pseudospins could prove to be better information carriers.

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