Revealing the Superior Electrocatalytic Performance of 2D Monolayer WSe₂ Transition Metal Dichalcogenide for Efficient H₂ Evolution Reaction

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H₂ evolution reaction (HER) requires an electrocatalyst to reduce the reaction barriers for the efficient production of H₂. 2D transition metal dichalcogenides (2D TMDs) have emerged as a pinnacle group of materials for many potential applications, including HER. In this work, a pristine 2D monolayer WSe₂ TMD is computationally designed using the first principle-based hybrid density functional theory (DFT) to investigate its structural, electronic properties and the electrocatalytic performance for HER. The possible Volmer-Heyrovsky and Volmer-Tafel reaction mechanisms for HER at the W-edge of the active site of WSe₂ are studied by using a nonperiodic finite molecular cluster model W₁₀Se₂₁. The study shows that the pristine 2D monolayer WSe₂ follows either the Volmer-Heyrovsky or the Volmer-Tafel reaction mechanisms with a single-digit low reaction barrier about 6.11, 8.41 and 6.61 kcal mol⁻¹ during the solvent phase calculations of H⁺-migration, Heyrovsky and Tafel transition (TS) states, respectively. The lower reaction barriers, high turnover frequency (TOF) = 4.24 × 10⁶ s⁻¹ and 8.86 × 10⁷ s⁻¹ during the Heyrovsky and Tafel reaction steps and the low Tafel slope 29.58 mV dec⁻¹ confirm that the pristine 2D monolayer WSe₂ might be a promising alternative to platinum group metals (PGM) based electrocatalyst.

1. Introduction

The fossil fuel has been used as a common energy source to satisfy the requirements of energy supply since the last century. However, its consumption is responsible for the emission of many hazardous environmental pollutants and greenhouse gases, resulting in significant climate change. It has an adverse effect on human health as the emissions are very harmful for our society. Therefore, there is an increasing demand for the exploitation of inexpensive, earth-abundant, clean and renewable energy sources that can replace the overutilization of carbon-based fossil fuels and meet the global energy crisis deprived of the emission of any environmental and health pollutants.[1,2] Hydrogen has significant energy content, carries high energy density in its molecular form (H₂), and is present enormously in the form of water and other organic and inorganic compounds. Thus, it is considered as a promising and efficient green energy carrier.[3–5] In today’s world, most commercially available H₂ fuel is manufactured by the steam reforming process. In this process, H₂ is produced along with carbon monoxide and carbon dioxide emissions like poisonous gases. The demerit of this process is that it has low energy efficiency for the conversion process and emits carbon-based unsafe byproducts.[6–8] An alternative way to produce clean and renewable H₂ is through the electrolysis of water with the passage of electricity through it.[7,9]

Overall electrolysis of water completes with two half-cell reactions: hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode.
Where M stands for the active site of the catalyst and MH_ads stands for the adsorbed hydrogen (H_ads) at the catalyst's active site. The complete evolution process of molecular hydrogen may follow either Volmer-Heyrovsky or Volmer-Tafel reaction pathways. The sluggish reaction rate of the HER in an alkaline solution originates from the additional water dissociation step that provides protons for the subsequent reactions, but this step does not occur in an acidic solution. Even for the most prominent catalyst, Pt, the catalytic activity in the alkaline medium is hindered by the sluggish water dissociation step, resulting in a reaction rate which is 2–3 orders of magnitude lower than that in the acidic solution.[12,13] An overpotential is required for the adsorption of the proton (H⁺) at the active site of the electrocatalyst and to reduce it into H₂ during the above-mentioned reaction pathways.[14] Reduction of this overpotential is the crucial part of the HER, and the same can be obtained with the use of an excellent electrocatalyst for the efficient production of H₂. Due to nearly zero overpotential, high exchange current density, and small Tafel slope of the platinum-group elements, i.e., noble metal-based electrocatalysts (such as Pt, Pd, etc.) in the acidic electrolyte, they have been adopted as the most active and stable electrocatalyst for the efficient production of H₂ through HER.[15] However, their high cost and low abundance for the commercial purpose bring constraints over their potential applications to meet the energy demand and have extensively motivated us to search for better and earth-abundant HER catalysts.[16] Hence, developing a cost-effective, earth-abundant, low Gibbs free energy change (∆G) during the TSs formation, i.e., the reaction barriers of HER and lower value of the Tafel slope are paramount important for the scalable production of clean and sustainable H₂ energy.[17]

On the other side, the 2D monolayer structure of transition metal dichalcogenides (TMDs) with their unique properties such as corrosion stability, tunability in the electronic properties and the possibility of defect engineering have brought an intense research in the scientific community for various applications.[18] Earth-abundant TMDs have the chemical formula of MX₂, where M is a transition metal atom such as Mo, W etc. and X is a chalcogen atom such as S, Se and Te. Different kinds of 2D TMDs, such as molybdenum disulfide (MoS₂), tungsten disulfide (WS₂), transition metal doped-MoS₂, etc., have shown HER catalytic performance with low over-potentials.[9] Therefore, they are a promising alternative to noble Pt metal-based electrocatalysts.[18] Hinnemann et al.[19] computationally found that the 2D monolayer MoS₂ TMD material has HER catalytic activities because of its nearly thermoneutral hydrogen adsorption energy. Recently, Huang et al.[16] performed a DFT[20–24] study on the Mo-edges (10T0) of the 2D monolayer MoS₂ TMD material to explore the HER mechanism, possible reaction pathway, and the reaction barriers by using a non-periodic cluster model system Mo₁₀S₂₁. Their theoretical study found that the Volmer-Heyrovsky mechanism is the thermodynamically favorable and convenient reaction pathway for H₂ formation, i.e., HER process.[16] Unfortunately, the 2D monolayer tungsten diselenide (WSe₂) has been ignored because of its lower electronic conductivity and mobility. However, due to its high activity, ultra-low thermal conductivity (0.05 W m⁻¹ K⁻¹), relatively lower band gap (~1.6 eV) and earth abundance, the 2D pristine WSe₂ has been recently identified as an efficient electrocatalyst for HER, although it has been less explored for HER catalytic performance compared to other chalcogens containing TMDs.[25] The 2D monolayer pristine WSe₂ TMD has three atom layers (Se-W-Se) in which the central layer of transition metal tungsten (W) is sandwiched in between two layers of selenium (Se) chalcogens. In the 2D monolayer WSe₂, each W atom in the middle basal plane is bonded with three Se atoms at the upper plane and three Se atoms at the lower plane through the covalent bonding, as shown in Figure 1. In other words, one Se atom at the top and bottom layer of the 2D monolayer WSe₂ is bonded with three W atoms at the middle basal plane through covalent bonding. A van der Waals (vdW)

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \tag{1}
\]

HER is the half-key reaction which includes the following steps[10,11]

**Volmer reaction:**
\[
\text{H}^+ + \text{M} + \text{e}^- \rightarrow \text{MH}_{\text{ads}} \quad \text{(In acidic medium)} \tag{2}
\]

**Heyrovsky reaction:**
\[
\text{MH}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{M} + \text{H}_2 \quad \text{(In acidic medium)} \tag{3}
\]

**Tafel reaction:**
\[
2\text{MH}_{\text{ads}} \rightarrow 2\text{M} + \text{H}_2 \tag{4}
\]

Figure 1. a) Top view and b) side view of the equilibrium structure of the periodic 2D monolayer WSe₂ material are shown here.
force separates different 2D WSe$_2$ layers of a bulk WSe$_2$ with Se terminating the inert basal plane (001).[38,36–39] Whereas, only the edges of the 2D monolayer WSe$_2$ are catalytically active sites for HER.[27]

The HER catalytic performance of any kind of 2D TMDs, such as 2D WSe$_2$ depends upon the density of exposed active edge sites,[28] hydrogen adsorption free energy ($\Delta G_{\text{H}}$), turnover frequency (TOF),[29] overpotential, Tafel slope, activation energy barriers, etc. Lowering the activation barrier energies through hydrogen adsorption and H$_2$ formation of an electrocatalyst has a paramount importance during the HER process. In this regard, we have theoretically and computationally investigated the HER catalytic activity of the pristine 2D monolayer WSe$_2$ TMD using the hybrid density functional theory (DFT)[20–22] method with the dispersion correction parameters to determine the reaction pathway for HER on the W-edge (10$ar{1}$0) of the WSe$_2$. Here, we computationally designed a 2D monolayer structure of the pristine WSe$_2$ TMD material, and studied the electronic band structure, total density of states (DOS), and electronic band gap with a potential application in electro-chemical water splitting reactions via HER. We employed first principles-based hybrid periodic DFT methods[20–24] with van der Waals (vdW) dispersion corrections (i.e., Grimme’s-D3 dispersion corrections)[22,30–33] to obtain the equilibrium geometries, structures, band structure, electronic bandgap ($E_g$) and total DOS to predict the electronic/material properties of the 2D monolayer WSe$_2$. We found that the 2D monolayer WSe$_2$ TMD is an excellent material for H$_2$ evolution with high electrocatalytic performance. It was computationally found that both the exposed Se-edge (10$ar{1}$0) and W-edge (10$ar{1}$0) edges of the WSe$_2$ are catalytic active for HER, and the (001) basal planes of the Se–W–Se trilayer of this material are exposed surfaces. We have described the W-edges of the 2D monolayer WSe$_2$ using a finite non-periodic molecular cluster model of W$_{10}$Se$_{21}$, which enables to integrate of the DFT accurately for calculating the reaction barriers while describing the solvation effect of water as solvent by considering the polarization continuum model (PCM). This theoretical approach determined the two-electron (2e$^-$) transfer chemical mechanism of HER through Volmer-Heyrovsky and Volmer-Tafel reaction pathways by estimating the changes of Gibbs free energy, i.e., relative free energy ($\Delta G$) (both the activation barriers and reaction intermediates), turnover frequency (TOF) and electronic structure and properties. A comparative description of the 2D monolayer WSe$_2$ toward HER has been given with other reported 2D TMDs and their alloys. The present computational DFT study of the pristine 2D monolayer WSe$_2$ shows that it has very low activation energy barriers during the Volmer step for the adsorbed hydrogen migration (H$^+$-migration) as well as the H$_2$ formation during both the Heyrovsky and Tafel reaction steps. Both the Volmer-Heyrovsky and the Volmer-Tafel reaction mechanisms have been considered here and both the pathways have very low activation energy barriers in both the solvent and gas phases found in the present computational study. The lowest activation energy barriers of the pristine 2D monolayer WSe$_2$ compared with other 2D TMDs enables it to use as a potential candidate for low-cost, earth-abundant and noble metal-free electrocatalyst for efficient production of H$_2$ through HER.

2. Methodology and Computational Details

The computational methods along with other parameters used during the theoretical study play a vital role to determine electrocatalytic activities for efficient HER. In the present study, a periodic 2D monolayer of the WSe$_2$ was computationally designed to investigate its structural and electronic properties with the aid of the first principle-based hybrid periodic DFT method with the dispersion corrections. Similarly, a non-periodic finite molecular cluster model W$_{10}$Se$_{21}$, corresponding to the 2D monolayer WSe$_2$ TMD was established and considered to study the HER mechanism at the active edges through the DFT calculations. Further discussions of the periodic and non-periodic systems are explained in detailed as follow.

2.1. Periodic DFT Calculations

The first principle-based periodic hybrid density functional theory (DFT) method was applied to obtain a symmetric 2D monolayer structure of the WSe$_2$. The equilibrium geometry with optimized lattice parameters of the symmetric 2D monolayer WSe$_2$ was obtained by using the first principle-based B3LYP-D3 (Becke, 3-parameter, Lee-Yang-Parr with Grimme’s-D3 dispersion correction)[30–33,34,35] method implemented in ab-initio based CRYSTAL17 suit code.[36–40] This B3LYP-D3 DFT method suffers less (or no) spin contaminations effect compared to the other post-Hartree-Fock (HF) methods which helps to provide an excellent calculations for geometry, energy and electron density.[36,35,46–51] Semi-empirical Grimme’s 3rd order dispersion correction (Grimme’s-D3) is taken account to encounter the non-bonding weak van der Waals (vdW) interactions among different layers and atoms to achieve a fine equilibrium geometry.[48–51] Triple-ζ valence polarization (TZVP) quality Gaussian types of basis set with Gaussian types of atomic orbitals (GTO) has been used for the Se atoms and Gaussian basis sets of W$_{CorA}$1996 has been used for the W atoms in the present computations.[53–56] The convergence criteria between two consecutive iteration steps for energy, force and electron density calculations was set with a threshold value of 10$^{-7}$ a.u.[55,56] In other words, a threshold value of 10$^{-7}$ a.u. was used for the convergence of forces, energy, and electron density for all cases. The periodicity in the z-direction of the crystal structure was ignored by keeping the height of the unit cell around =500 Å, i.e., the vacuum region of approximately 500 Å was considered in the present calculations to accommodate the vacuum environment. The vacuum region of 500 Å was set to avoid the interlayer interaction between two consecutive layers in the z-direction implemented in the CRYSTAL17 suite code.[35–40,57] VESTA visualization software is used for the provision of analysis and graphical representation of the periodic optimized structures.[58,59] The equilibrium periodic 2D monolayer structure of the WSe$_2$ material is shown in Figure 1. The equilibrium geometry with the lattice parameters (i.e., lattice constants, symmetry, and atomic positions) of the 2D monolayer WSe$_2$ TMD were further utilized to calculate its electronic properties such as electronic band structure, electronic band gap ($E_g$) and total electron density of states (DOS). The k-mesh grid is sampled on 15 × 15 × 1 Monkhorst-pack for all
the integrations of the first Brillouin zone during all the computations with a resolution about $2\pi \times 1/60$ Å$^{-1}$ for both the optimization and material/electronic properties calculations.

### 2.2. Nonperiodic DFT Calculations

A non-periodic finite molecular cluster model system $W_{10}Se_{21}$ of the 2D WSe$_2$ has been constructed to explore the HER mechanism on the active surface of the 2D monolayer WSe$_2$ TMD. Figure 2a shows how to extract the triangular non-periodic finite molecule cluster model system $W_{10}Se_{21}$ from the periodic 2D monolayer WSe$_2$ to expose its either W-edges or Se-edges. The upper black dotted horizontal line represents the termination along W-edge ($10\overline{1}0$) and the bottom black dotted horizontal line denotes the termination along Se-edge ($\overline{1}010$) as shown in Figure 2a. The straight triangle represents the non-periodic finite cluster model terminated along the Se-edge ($\overline{1}010$) and the upside-down triangle corresponds to the non-periodic cluster model terminated along the W-edge ($10\overline{1}0$). Figure 2b–d signifies the structure of the molecular cluster model system $W_{10}Se_{21}$ containing 10 central tungsten (W) metal atoms in a single triangular plane and 21 selenium (Se) atoms (9 Se atoms in the central W plane and 6-6 Se atoms at the top and bottom plane of the central W plane) followed by the previous molecular structure of MoS$_2$.[9,16] The logic behind developing such finite molecular cluster is that: i) it replicates our parental Se-W-Se tri-layer of the pristine 2D monolayer WSe$_2$ with the catalytically inert basal plane (001) and catalytically active W-edges ($10\overline{1}0$) and Se-edges ($\overline{1}010$); ii) it provides feasibility of doping engineering as the W metal atoms can be substitutionally doped with other atoms by 10% variation of each W atom substitution and the same procedure can be adopted for the Se atoms as well, and iii) this finite molecular cluster model system $W_{10}Se_{21}$ provides a viability of introducing protons (H$^+$) and electrons (e$^-$) separately which are essential to explore free energies as a function of electrochemical potential and pH values.[9,16]

A non-periodic DFT method has been used for all the theoretical calculations to explore the HER process on the surfaces of the pristine 2D monolayer WSe$_2$ material. In the finite molecular cluster model, each W atom in the basal plane (001) has +4 oxidation state and each of them creates six bonding with six adjacent Se atoms (i.e., three Se atoms at the lower plane and three Se atoms at the upper plane). Due to this configuration, a stabilized structure is resulted in which each W-Se bonding have a 4/6 = 2/3 electron contributions in the inert basal plane. The stabilization of the molecular cluster model also can be understood from the oxidation state of the Se atoms in the basal plane. Each Se atom has -2 oxidation state and creates bonding with 3 W atoms that gives a contribution of 2/3 electrons toward each W–Se bonding in the basal plane. Again, the edges of the molecular cluster model are stabilized with the 2 local electron W-Se bonds with a single electron contribution towards four W–Se bonds in the basal plane, as shown in Figure 2. This 14/3 {i.e., $2 \times 1 + [4 \times (2/3)]$} contribution of electrons towards the W–Se bonds of the edge W atom is satisfied with the d$^2$ configuration of one W atom and d$^1$ configuration of two W atoms at the edges. With this...

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**Figure 2.** a) Ball-and-stick style top view of the Se–W–Se trilayer periodic 2D monolayer WSe$_2$, the upper and lower black dotted horizontal lines represent the terminations along W and Se-edges, respectively. The purple colored up straight triangle represents the non-periodic molecular cluster with active Se-edge ($\overline{1}010$) termination and the upside-down purple triangle represents the non-periodic molecular cluster with active W-edge ($10\overline{1}0$) termination. b) Top view of the designated $W_{10}Se_{21}$ non-periodic triangular molecular cluster of the 2D monolayer WSe$_2$. c) Schematic representation of molecular cluster model system. (d) Side view of the chosen $W_{10}Se_{21}$ nonperiodic triangular molecular cluster of the 2D monolayer WSe$_2$ TMD are shown here.
configuration, a stabilized molecular cluster model with the periodicity 3 is achieved that derives the molecular cluster model having three edges without any unsatisfied valency. Thus, we considered a molecular cluster \( W_{10}Se_{21} \) model system (noted by \([WSe_2]\)) to represent the Se-terminated W-edges of 2D monolayer WSe\(_2\) TMD shown in Figure 2, and this \( W_{10}Se_{21} \) molecular cluster model system is good enough to explain the HER process.

All the required electronic and thermodynamic properties of the different reaction steps involved in this HER mechanism have been calculated by using Minnesota 2006 local functional (M06-L)[60] DFT method. M06-L is a local spin-specific kinetic energy density \( \tau_{\alpha}(\mathbf{r}) \), where \( \sigma=\alpha,\beta \) and \( \mathbf{r} \) = point in real space) generalized gradient approximation (GGA) method known as Minnesota DFT method.

\[
\tau_{\alpha}(\mathbf{r}) = \frac{1}{Z} \sum_{\mathbf{r}} \nabla \psi_{\alpha}(\mathbf{r}) \nabla \psi_{\alpha}(\mathbf{r}) + \alpha_i \psi_{\alpha}(\mathbf{r}) + \beta_i \psi_{\alpha}(\mathbf{r})
\]

(5)

where, \( \psi_{\alpha} \) represents spatial part of an occupied Kohn-Sham (KS) spin-orbital, \( n_{\alpha} \) is the number of occupied spin orbitals of the corresponding spin \( \sigma \).[61] The significances of using M06-L local functionals are: I) they are computationally cost-effective compared to non-local functionals for the molecule or the system containing large number of atoms considering density-fitting algorithms using Gaussian basis sets.[62-64] II) This M06-L method gives more accurate and reliable energy barriers and bond energies in the case of reaction mechanism for the systems containing transition metals (TMs) like Mo, W, etc., in which density-based exchange functionals describe static correction much better than the HF exchange.[65,66] DFT is widely used for large systems containing TMs as it describes electron correlation effects and has advantage over the post HF methods.[9,24,31,67–70]

Double-\( \zeta \) Pople-type Gaussian basis set 6-31+G\(^{**}\) has been used for the selenium (Se), hydrogen (H) and oxygen (O) atoms, and LANL2DZ (Los Alamos National Laboratory 2 double-\( \zeta \) basis set with effective core potentials (ECPs) for the W atoms)[70-72] The ECPs were used to replace the inner core electrons of the W atoms in the present calculations.[71-73] A harmonic vibrational frequency analysis has been carried out to confirm the stable minima of the quantum systems with the successful elimination of imaginary frequencies and to locate the transition states (TSs) during the HER mechanism. Gaussian16 Suite code was used to obtain the equilibrium structures and TSs of the different intermediates resulted during the HER mechanism of the 2D monolayer WSe\(_2\) system.[74-76] All the optimized stable geometries of different steps involved in the HER along with the equilibrium TSs are presented with the help of ChemCraft molecular visualization software.[77]

Polarization continuum model (PCM) analysis has been performed at the equilibrium geometry of solvent radius 1.4 Å and H\(_2\)O with a dielectric constant \( \varepsilon = 78.34 \) at 298.15 K temperature[78,79] to encounter the solvation effects in the present calculations.[78] Previously, it was theoretically reported that the Gibbs free energy (G) of the solvated proton (H\(^+\)) was obtained to be \(-271.86 \) kcal mol\(^{-1}\).[80] Later on, with the further theoretical study, the Gibbs free energy of the H\(^+\) was found to be \(-270.3 \) kcal mol\(^{-1}\) which is in well consistent with the previously reported value.[16] Tissierandier et al. theoretically estimated this value by taking the summation of gas-phase Gibbs free energy (G) value of H\(^+\) at 1 atm (G (H\(^+\), 1 atm) = H – TS = 2.5 kBT – T × 26.04 = –6.3 kcal mol\(^{-1}\)) and empirical hydrogen energy (G (H\(^+\), 1 atm → 1 M)) = −264.0 kcal mol\(^{-1}\)). The free energy of an electron by using standard hydrogen electrode (SHE) at pH = 0 is given as \( G(e^-) = G(\frac{1}{2}H_2) - G(H^+) \), where the Gibbs free energy of the hydrogen molecule (\( G(H_2) \)) for our calculation was found computationally by performing M06-L local functionals DFT calculations and the free energy of proton (G(H\(^+\))) was taken from the previously reported values.[16]

### 2.3. Theoretical Calculations and Equations

The electrocatalytic performances of the 2D monolayer WSe\(_2\) TMD have been characterized by the computations of the changes of Gibbs free energy (\( \Delta G \)) for H\(_2\) adsorption and reaction barrier during the TSs formation on the (\( \bar{T}0\bar{T}0 \)) Se-edges and (\( 10\bar{T}0 \)) W-edges of the TMD. The changes of free energy (\( \Delta G \)), enthalpy (\( \Delta H \)), and electronic energy (\( \Delta E \)) in both the gas phase and solvent phase for all the intermediates and TSs of the HER have been calculated by the following equations.

\[ \Delta G = \sum G_{\text{Product}} - \sum G_{\text{Reactant}} \]  

(6)

\[ \Delta H = \sum H_{\text{Product}} - \sum H_{\text{Reactant}} \]  

(7)

\[ \Delta E = \sum E_{\text{Product}} - \sum E_{\text{Reactant}} \]  

(8)

where \( \Delta E \) for each step participating in the HER were found computationally by the following expression.

\[ E = E_{\text{DFT}} + E_{\text{ZPE}} + \int C_v \, dT - TS \]  

(9)

where, \( E_{\text{DFT}} \) stands for the ground state electronic energy calculated by the DFT method, \( E_{\text{ZPE}} \) represents the zero-point vibrational energy, \( C_v \) is the lattice-specific heat capacity at constant pressure, \( S \) represents the entropy of the system and \( T \) corresponds to the temperature at the absolute scale (here, \( T = 298.15 \) K throughout our calculations).

### 3. Results and Discussion

#### 3.1. Equilibrium Periodic 2D Monolayer Structure Calculations

To acquire the fundamental understanding of the equilibrium geometry of the pristine 2D monolayer WSe\(_2\) material, we have computationally designed a 2D monolayer slab of the WSe\(_2\) TMD, which has P-6m2 hexagonal 2D layer symmetry (layer group number is 78). This periodic 2D slab corresponds to the periodic symmetry along the x and y directions representing the hexagonal 2D layer system with respect to the vacuum (w.r.t. vac.) space along z-axis. In other words, there is no symmetry along z-axis. The hybrid periodic DFT-D calculation shows that the equilibrium lattice parameters are about \( a = b = 3.23 \) Å and the interfacial angle between them is \( \gamma = 120^\circ \). The equilibrium structure of the pristine 2D monolayer WSe\(_2\) TMD is depicted...
in Figure 1. The equilibrium average W–Se bond length between W and Se atoms in the 2D slab WSe$_2$ is about 2.50 Å which is well harmonized with previously reported results$^{[62,63]}$ and the in-plane bond angle < Se–W–Se is about 83.61° and the out-plane bond angle < Se–W–Se is found to be 80.42°. This in-plane bond angle < Se–W–Se is in well consistent with the previously reported value of 83.80° calculated for the 3D bulk crystal structure of the WSe$_2$.$^{[81]}$ In short, the equilibrium lattice parameters such as the lattice constants (a and b), interfacial angle γ, layer group symmetry and the equilibrium average bond length W–Se of the 2D monolayer WSe$_2$ are found to be well consistent with the previously reported values, and they are summarized in Table 1.

3.2. Electronic Properties Calculations

The electronic properties calculations (i.e., electronic band structures, energy bandgap ($E_g$), position of the Fermi level ($E_F$), and total density of states (DOSs)) have been computed to explore the electronic/materials properties with the contribution of electrons toward the electrocatalytic activity of the pristine 2D monolayer WSe$_2$ as shown in Figure 3. The present DFT-D (i.e., B3LYP-D3) calculation shows that the pristine 2D monolayer WSe$_2$ is a pure semiconductor with a bandgap ($E_g$) energy about 2.39 eV, as depicted in Figure 3. To obtain the equilibrium electronic band structures of the pristine 2D monolayer WSe$_2$ material, total eight numbers of energy bands around the Fermi energy level ($E_F$) have been computed and drawn in a specific direction of irreducible Brillouin zone by choosing Γ-M-K-Γ high symmetric points as depicted in Figure 3a, which is consistent with the original 2D layer group symmetry of the WSe$_2$ TMD material. It should be mentioned here that the electrostatic potential calculations have been included in the present computations for the 2D monolayer calculations of the WSe$_2$ TMD, i.e., the energies of both the band structures and total DOS are reported with respect to the vacuum (w.r.t. vac.). The Fermi energy level ($E_F$) was found at −6.59 eV which is very close to the top of valence band (VB), and a direct electronic band gap was at K point in the band structure calculations which was later confirmed by the total DOS calculations. Figure 3b represents the total density of states of the pristine 2D monolayer WSe$_2$ in which the maxima of the valence band (VB) and the minima of the conduction band (CB) were found at −6.59 eV and −4.20 eV, respectively. Here, the $E_F$ is near to the maxima of the VB and the electron density of the minima of the CB is about 2.39 eV far from the $E_F$ and the difference between these values is equal to the energy band gap ($E_g$ ≈ 2.39 eV). The ground state electronic configurations of the W and Se atoms are given by [Xe] 4f$^{14}$ 5d$^{4}$ 6s$^{2}$ and [Ar] 4s$^{2}$ 3d$^{10}$ 4p$^4$, respectively, so each W atom has four unpaired up spin electrons in the 5d$_{xy}$, 5d$_{yz}$, 5d$_{zx}$ sub-shells and it has a vacant 5d$_{z^2}$ sub-shell of the 5d orbital. Similarly, each Se atom has paired spins in 4p$_x$ subshell and two single unpaired spin electrons in 4p$_y$ and 4p$_z$ subshells of the 4p orbital. As both the W and Se atoms have unpaired spins in their respective higher orbitals, so the partial density of states (PDOS) calculations have been performed for both to understand the availability of states for occupation in each case. The PDOS calculations of the W atom indicate that a significant contribution of the DOS goes toward the conduction band electron density of states of the total DOS. However, the contribution of the W atom towards the valence band electron density of states of the total DOS is comparatively

![Figure 3](https://www.advancedsciencenews.com/2202075/2202075_6.png)

**Figure 3.** a) Electronic band structure; b) Total DOSs of the pristine 2D monolayer WSe$_2$; and partial density of states calculation of the c) W atoms, d) Se atoms, e) d-orbital of the W atoms are shown here.

**Table 1.** Equilibrium lattice parameters and the average bond length of optimized 2D WSe$_2$.

| Parameters | Optimized parameters | Previously reported values | Refs. |
|-----------|---------------------|---------------------------|-------|
| a (in Å)  | 3.23                | 3.32, 3.29                | $^{[82]}$ |
| b (in Å)  | 3.23                | 3.32, 3.29                | $^{[82]}$ |
| α (in°)   | 90                  | 90                        | $^{[82]}$ |
| γ (in°)   | 120                 | 120                       | $^{[82]}$ |
| Symmetry  | P 6mm               | P 6mm                     | $^{[83]}$ |
| W–Se average bond length (in Å) | 2.50 | 2.55, 2.53 | $^{[82]}$ |
less, as shown in Figure 3c. From the partial density of states calculations of the Se atom, similarly, it can be observed that an important contribution of the density of states in the total DOSs arises due to the Se atoms. Figure 3e elaborates that the participation of 5d orbital of the W atom is mainly responsible for the DOSs calculations of the W atom in the 2D monolayer WSe$_2$. We have shown that the pristine 2D monolayer WSe$_2$ could be a better candidate for HER catalyst since the electronic properties calculations show that the pristine 2D monolayer WSe$_2$ is a direct band gap semiconductor with an energy band gap (E$_g$) about 2.39 eV. The calculated bandgap is well consistent with the earlier reported results, and even before this study, several pristine 2D TMDs such as MoS$_2$, WSe$_2$, etc. have been used as an electrocatalyst for HER.$^{[8,16,84]}$ The bandgap energy of semiconductors tends to decrease with increasing temperature. When temperature increases, the amplitude of atomic vibrations increases leading to larger interatomic spacing. At room temperature, some covalent bonds of the TMDs can break especially near to the edges (here, the edges of the 2D WSe$_2$ TMD), and the semiconductor behaves like a conductor at $T = 298.15$ K. A semiconductor catalyst processing electrocatalytic activities should absorb protons (H$^+$) and electrons (e$^-$) simultaneously onto the surface, resulting in the transition of semiconductor materials. The electrocatalytic performances of the 2D single-layer WSe$_2$ TMD have been investigated at room temperature by computing the thermodynamical potentials and activation barriers considering a finite nonperiodic molecular cluster model system. It is well documented that loading electrocatalysts on semiconductor electrodes play significant roles in accelerating the HER kinetics, suppressing surface recombination, reducing overpotentials needed to accomplish HER, and extending the operational lifetime of semiconductors.$^{[9,16,84]}$ The 2D monolayer WSe$_2$ TMD may also be a suitable electrocatalyst for HER, so in the next section, we have studied the HER mechanism by taking the non-periodic finite molecular cluster system of the 2D WSe$_2$ TMD. It has been experimentally proved that the pristine 2D monolayer tungsten selenide (WSe$_2$) TMD has emerged as a promising electrocatalyst for hydrogen evolution reaction. However, there was no theoretical and computational investigation about the catalytic activities of the 2D monolayer WSe$_2$ TMD to support or validate the experiments. In this study, we have investigated how the 2D monolayer WSe$_2$ is catalyzing the HER process, and it could be a promising candidate for an effective HER in the present work electrocatalyst. A detailed description and analysis have been provided in the present investigations.

### 3.3. HER Mechanism and Thermodynamic Properties Calculations

Overall electrocatalytic HER follows either Volmer-Heyrovsky or Volmer-Tafel reaction mechanisms. The study and analysis of reaction barriers during the hydrogen adsorption (Volmer reaction step), H$^+$-migration and the hydrogen molecule desorption (either in the Heyrovsky reaction step or in the Tafel reaction step, i.e., $H_2$ formation during the HER process) processes are required to explain the electrochemical activities for efficient $H_2$ evolution reactions of the electrocatalyst. In accordance with the above processes, two HER pathways are possible namely; (i) Volmer-Heyrovsky mechanism pathway in which Volmer reaction step (in short, $M + H^+ + e^- \rightarrow MH^{ads}$ where protons (H$^+$) interact with the electrons, and the hydrogen atoms get adsorbed on the active region of the catalyst; where M represents the active sites of the catalyst). This reaction pathway is accompanied by the migration of H$^+$ from the Se atom site to the W transition metal atom site after the proton gets adsorbed to the active site of the catalyst. The present DFT calculations show that the first H energetically prefers to form a bond with the Se atom, as the direct hydrogen adsorption at the W-edge site is not thermodynamically favorable in the early stage of HER.$^{[56,76,85]}$ Because the Se atoms are located at the edges in the 2D monolayer WSe$_2$ slab structure and the same finite nonperiodic molecular cluster model system, and the basal planes of the TMD are more “inactive” than the edges. The edge sites play a major role in determining the overall activity, especially for catalysts with inactive basal planes. In general, the edge of the 2D monolayer WSe$_2$ slab is more reactive than the inert basal plane. However, for metal basal plane catalysts, the binding energy may be the same. The large distance between hydrogen atoms with low coverage and the rearrangement of Se atoms in 2D monolayer WSe$_2$ slab upon hydrogen adsorption suggests that the weakening of H bonding upon successive H adsorption is due to the limited number of basal states and the corresponding changes in geometry. A catalyst should bind moderately (not too strong or too weak) to the reagents and intermediates so that they are likely to adsorb to the surface, allowing the reaction to occur. However, if the catalyst binds the intermediates or products too strongly, the products formed on the catalyst cannot desorb, leaving the catalyst inhibited. Thus, the Sabatier principle states that the optimal catalyst binds a key intermediate strongly enough so that the reagents will likely bind and react, but weakly enough so that the product will easily desorb.$^{[86]}$ With the help of the Sabatier relationship, one can relate the relative free energy of the hydrogen with the exchange current density during HER. The change of Gibbs free energy should be neither too much negative nor too much positive because if there is a more negative value of $\Delta G$ then, hydrogen will bond more strongly to the surface of the catalyst, making the desorption step more difficult and if there is the more positive value of $\Delta G$ then the hydrogen bond with the catalyst will be weak due to which the adsorption step will be difficult. Therefore, the change of Gibbs free energy of the catalyst should appear as close to zero as possible.

We have used a cluster model $W_{10}Se_{21}$ for the present work for the HER. In this cluster, we have calculated the adsorption energy of hydrogen on the surface of the catalyst. The site which is more active for hydrogen adsorption will favor the adsorption of hydrogen easily. We have calculated hydrogen adsorption at both the sites, Se and W. First, we calculated the relative hydrogen adsorption free energy at the Se site, which results the formation of $[WSe_2]HSe$ as an intermediate (where the subscript Se indicates that the hydrogen is bound to the Se atom), and it has been computationally found that the change of free energy ($\Delta G$) is $-1.91$ eV when H adsorption occurs at the Se site of the catalyst. The equilibrium bond length of the Se–H in the equilibrium structure of the intermediate $[WSe_2]HSe$ is 1.47 Å. Here, we found a negative change in free energy

\[ \Delta G = -1.91 \text{ eV} \]
which leads to hydrogen strongly prefer to create bonds with the selenium. Now, we have also calculated hydrogen adsorption at the W site and it has been found that the change in free energy (ΔG) is –1.78 eV which is higher than the previous one. The equilibrium bond length of the W–H in the intermediate [WSe2]HSe is 1.72 Å. The values of ΔG are negative in both the cases during H adsorption at the Se and W sites. But at the Se site the change in free energy is slightly more negative compared to the W site, and W is inside the 2D monolayer WSe2 and Se is on the surface. So, the first H energetically prefers to form a bond with the Se atom, as the direct hydrogen adsorption at the W-edge site is not thermodynamically favorable in the early stage of HER. This is well harmonized with the other reported TMDs and Janus TMDs.[57,76,85]

In the Heyrovsky reaction step, one adsorbed hydride (H•) at the transition metal site (here W) reacts with one solvated proton of the adjacent water to form one H2 molecule. The second reaction mechanism follows the Volmer–Tafel reaction pathway, in which after the completion of Volmer reaction step, Tafel reaction step proceeds through one H• at the transition metal site W recombines with one H• at the Se site to form H2 molecule. Our nonperiodic finite triangular molecular cluster model W10Se21 system of the pristine 2D monolayer WSe2 has the provision to introduce or remove protons (H+) and electrons (e−) individually to the system and to account the free energies of different intermediates resulted during the HER process. To enable the use of the most accurate DFT for reaction barriers while describing solvation effects, we used this W10Se21 cluster model system of the 2D monolayer WSe2. This allows us to consider the introduction of protons (H+) and electrons (e−) separately and report free energies as a function of electrochemical potential and pH. Using molecular clusters to model a periodic system for determining reaction mechanisms allows more flexibility in the accuracy of the methods. As the complete HER process may proceed either through Volmer–Heyrovsky reaction mechanism or via Volmer–Tafel reaction mechanism, so the energy barriers of various reaction steps need to be inspected to trace the rate-limiting steps and to explain the HER process. Li et al.[87] and Lie et al.[9] reported that, because of the lower hydrogen adsorption free energies of transition metal based HER electrocatalyst, Volmer–Heyrovsky reaction mechanism is the most promising reaction mechanism for H2 evolution. As the 2D monolayer WSe2 material has been less explored toward its electrocatalytic performance.[25] so our study has been extended for both the Volmer–Heyrovsky and Volmer–Tafel proposed reaction pathways to predict the most predominant mechanism and the HER activity of the pristine 2D monolayer WSe2 TMD material.

3.3.1. Volmer–Heyrovsky Reaction Mechanism

Volmer–Heyrovsky mechanism follows a two-electron (2e−) transfer process, and the complete reaction processes participating in this proposed reaction pathway (when the HER occurs at the Se-terminated W-edges of the 2D monolayer WSe2 material) are given schematically in Figure 4. This multistep electrode reaction schematic representation includes the possible intermediates and the transition states (TSs) formed during the HER process. During the Volmer reaction step, the protons (H+) and electrons (e−) simultaneously are absorbed in the catalyst, and then the migration of the hydride ion (H•) occurs which is the crucial step during the H•-migration reaction. Similarly, in the Heyrovsky reaction step, formation of H2 plays the vital role which is accomplished by the involvement of H+ at the transition metal site along with the requirement of one proton from the adjacent hydronium ion (H3O+). As shown in Figure 4, the complete H2 evolution process is accomplished with the introductions of individual electrons (e−) and protons (H+) in the system during HER process. It is necessary to inspect the first most stable structure of the nonperiodic finite cluster model W10Se21 system of the WSe2 TMD along with the other structures resulted with the successive addition of each extra number of electrons and protons in order to understand the variation of free energies between the intermediates and eventually discover the possible lowest reaction barrier pathway. The detailed reaction steps involved in this proposed HER pathway are described as follow.

1. At the standard hydrogen electrode (SHE) and pH = 0, the [WSe2] material is the most stable state with bare neutral W-edge, which becomes the basis for our thermodynamic potential calculations. The finite molecular cluster W10Se21 is noted by [WSe2] in short. The equilibrium structure is shown in Figure 5a.

2. To start the water splitting reactions by HER process, one electron is absorbed on the surface of the [WSe2] resulting a negatively charged cluster [WSe2]−1 solvated in water with a delocalized electron on its surface. The first reduction potential of this proposed reaction pathway to obtain [WSe2]−1 from the pristine [WSe2] with the introduction of a single electron is about –667.16 mV computed by the DFT method. The equilibrium geometry of the [WSe2]−1 is displayed in Figure 5b.

Here the free energy of the electron (e−) is calculated through the expression $G(e^{-}) = G(\frac{1}{2}H_{2}) - G(H^{+})$. The free energy of proton, $G(H^{+})$ is –274.86 kcal mol\(^{-1}\) taken from previously reported value by Tissandier et al.[80] whereas the free energy of the hydrogen molecule, $G(H_{2})$ is obtained by the present DFT calculations and the value is about –735.27 kcal mol\(^{-1}\) giving the free energy of electron $G(e^{-})$ about –92.78 kcal mol\(^{-1}\).

3. The first hydrogen strongly prefers to bind the Se-edge rather than W atom.[8] so adding a proton (H+) to the Se-edge having one extra electron [WSe2]−1 results [WSe2]HSe as an intermediate (where the subscript Se indicates that the hydrogen is bound to the Se atom) with an energy cost about 6.15 kcal mol\(^{-1}\). The equilibrium bond length of the Se–H in the intermediate [WSe2]HSe is 1.47 Å, and the equilibrium geometry of the complex is displayed in Figure 5c.

4. Further adding one more electron to the [WSe2]HSe, the second reduction takes place resulting [WSe2]HSe\(^{-1}\) (as shown in Figure 5d) with a second reduction potential about –1040 mV (i.e., –1.04 V).

5. In the next step, the hydride ion (H•) adsorbed at the Se-site migrates to the adjacent W-site forming a transition state
(TS) of the \([\text{WSe}_2]H_W^{-1}\) called as \(H^*\)-migration reaction step also known as \(H^*\)-migration transition state (TS) or Volmer transition state (TS1). This is the first TS appeared during the HER process. A harmonic vibrational frequency analysis has been carried out to find out the TS and intrinsic reaction coordinates (IRC) calculations\cite{44,45,88} have been performed to confirm the TS1. This TS1 is detected to have a single imaginary vibrational frequency when the \(H^*\) migrates from the Se-site to W-site. The equilibrium geometry of the TS1 is displayed in Figure 5e. More interestingly, the present DFT study shows that the activation energy barrier in the gas phase calculation of the \(H^*\) migration reaction to form the TS1 in the case of the pristine 2D monolayer WSe\(_2\) is about \(\Delta G = 2.67\) kcal mol\(^{-1}\).
The solvation effect during the HER is incorporated through the polarization continuum model (PCM). In the present DFT-D calculations, we found that the energy barrier of the H*-migration or Volmer transition state (TS1) representing H*-migration from the Se site to the W site is about 6.11 kcal mol⁻¹ computed in the solvent phase, i.e., water environment. This low value of the energy barrier of TS1 in both the solvent and gas phases calculations shows better hydrogen migration/adsorption than other TMDs. In practice, the actual HER happens in solvent phase, so first we have studied the reaction in gas phase and then, we have further studied the solvent

![Figure 5. The equilibrium geometries of the non-periodic molecular cluster model of the a) pristine W₁₀Se₂₁ (noted by [WSe₂]), b) [WSe₂]⁻¹, c) [WSe₂]H⁻, d) [WSe₂]H⁺, e) H*-migration or Volmer transition state (TS1) representing H*-migration from the Se site to the W site, f) [WSe₂]H⁺, g) [WSe₂]H⁺H⁺, h) [WSe₂]H⁺H⁺, i) side-view of Heyrovsky transition state (TS2) representing the H₂ formation, and j) [WSe₂]⁺ are shown here.](image-url)
Table 2. Energy changes (ΔE, ΔH and ΔG) for different intermediates and transition states (TSs) during Volmer-Heyrovsky reaction mechanism in the gas phase calculations are tabulated here. The units are expressed in kcal mol\(^{-1}\).

| System or reaction intermediates/TSs | ΔE [in kcal mol\(^{-1}\)] | ΔH [in kcal mol\(^{-1}\)] | ΔG [in kcal mol\(^{-1}\)] |
|--------------------------------------|---------------------------|---------------------------|---------------------------|
| WSe\(_2\) \(\rightarrow\) [WSe\(_2\)]\(^{-1}\) | 15.94                     | 16.13                     | 15.38                     |
| [WSe\(_2\)]\(^{-1}\) \(\rightarrow\) [WSe\(_2\)]H\(_{\text{Se}}\) | –6.18                     | –6.06                     | –6.15                     |
| [WSe\(_2\)]H\(_{\text{Se}}\) \(\rightarrow\) [WSe\(_2\)]H\(_{\text{Se}}\) | 23.11                     | 23.16                     | 24.09                     |
| [WSe\(_2\)]H\(_{\text{Se}}\) \(\rightarrow\) H\(^{+}\) –migration TS1 | 2.79                      | 2.67                      | 2.67                      |
| H\(^{+}\) –migration TS1 \(\rightarrow\) [WSe\(_2\)]H\(_{\text{w}}\) | –15.45                    | –15.53                    | –15.61                    |
| [WSe\(_2\)]H\(_{\text{w}}\) \(\rightarrow\) [WSe\(_2\)]H\(_{\text{w}}\) | –9.48                     | –9.31                     | –9.49                     |
| [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) \(\rightarrow\) [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) \(-4\text{H}_2\text{O}\ ·\text{H}^{+}\) | –24.96                    | –24.76                    | –11.17                    |
| [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) \(-4\text{H}_2\text{O}\ ·\text{H}^{+}\) \(\rightarrow\) Heyrovsky TS2 | 5.73                      | 5.64                      | 6.24                      |
| Heyrovsky TS2 \(\rightarrow\) [WSe\(_2\)]H\(_{\text{w}}\)\(^{1}\) | 8.48                      | 9.64                      | –6.27                     |

phase calculations taking the equilibrium geometries of all the reaction intermediates/TSs computed in gas phase. PCM calculations are performed at the equilibrium geometries of the systems involved in the subject reaction computed in gas phase. Reaction barriers in solvent phase are usually larger than the values in gas phase. If we add the solvent parameter, the energy changes a lot explicitly considering the interaction between the solvent and reactants. It is two different phases with completely different properties. Different types of chemical bonds and interactions are formed during the solvation process, such as hydrogen bonds, ion-dipole interactions and weak van der Waal (vdW) forces.

6. The energy cost to from the [WSe\(_2\)]H\(_{\text{w}}\)\(^{-1}\) complex from the TSI is found about ΔG = –15.61 kcal mol\(^{-1}\) computed by the DFT method, and the equilibrium geometry can be found in Figure 5f. The changes of electronic energy (ΔE), relative enthalpy (ΔH) and Gibb’s free energy (ΔG) during the HER process in various reaction steps computed by the M06-L DFT method are reported in Table 2.

7. One more H\(^{+}\) from the solvent medium to the Se-site of the [WSe\(_2\)]H\(_{\text{w}}\)\(_{\text{Se}}\) complex has been added to form the [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) (the subscripts W and Se at the H indicate that the one hydrogen is bound to the W atom and the other hydrogen is bound to the Se atom as depicted in Figure 5g) with an energy cost about –9.49 kcal mol\(^{-1}\) obtained by the DFT computation as shown in Table 2. The equilibrium structure of the [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) complex was found to have the equilibrium bond lengths, W–H about 1.72 Å and Se-H about 1.47 Å, respectively, computed by the same DFT method. All the optimized equilibrium structures of the intermediates and the TSs involved in the subject reaction are given in Figure 5.

8. From the [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) complex, either the Heyrovsky or the Tafel reaction process may proceed for the H\(_2\) evolution. In the case of Heyrovsky reaction process, we explicitly add a hydronium water cluster (4H\(_2\)O \(\cdot\)H\(^{+}\), as shown in Figures 5h and 6) near to the active site of the W\(_{\text{Se}}\)\(_{21}\) (i.e., [WSe\(_2\)]) nonperiodic molecular cluster with one H\(^{+}\) at the transition metal W site and another H\(^{+}\) at the Se site resulting the [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) \(\cdot\)4H\(_2\)O \(\cdot\)H\(^{+}\) complex with an energy cost about ΔG = –11.17 kcal mol\(^{-1}\). The equilibrium structure of the [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) \(\cdot\)4H\(_2\)O \(\cdot\)H\(^{+}\) complex is depicted in Figure 5h.

9. To proceed further HER, the second transition state has been formed as known as Heyrovsky’s transition state (TS2) shown in Figure 5i. The second TS known as Heyrovsky TS2 results from the [WSe\(_2\)]H\(_{\text{w}}\)H\(_{\text{Se}}\) \(\cdot\)4H\(_2\)O \(\cdot\)H\(^{+}\) in which H\(^{+}\) from the W-site and H\(^{+}\) from the hydronium water cluster recombine to evolve as H\(_2\) and gets separated from the system as depicted in Figure 5i. The formation of H\(_2\) during the reaction in TS2 is highlighted in red dotted circle in Figure 5i. The activation energy barrier of the Heyrovsky TS2 is about 6.24 kcal mol\(^{-1}\) computed in the gas phase. It should be mentioned here that in acidic media, the Volmer–Heyrovsky reaction mechanism proceeds via two proton-coupled electron transfer (PCET) steps; 1) electrosorption of a solvated proton, i.e., the Volmer reaction, followed by 2) an Eley–Rideal-type recombination of the adsorbed hydrogen (H\(^{\bullet}\)) and another solvated proton to form molecular hydrogen, the Heyrovsky reaction.

\[
\left[(\text{H}_2\text{O})_n \cdot \text{H}^{\bullet}\right] + e^- \rightleftharpoons \text{H}^{\bullet} + (\text{H}_2\text{O})_n \quad (10)
\]

\[
\left[(\text{H}_2\text{O})_n \cdot \text{H}^{\bullet}\right] + \text{H}^{\bullet} + e^- \rightleftharpoons \text{H}_2 + (\text{H}_2\text{O})_n \quad (11)
\]

In the preceding, the solvated proton complex is denoted by \([(\text{H}_2\text{O})_n \cdot \text{H}^{\bullet}\)]\(^{+}\), where \(n = 1, 2, \) and 4 are recognized as the hydronium (\(\text{H}_2\text{O}^+\)), Zundel (\(\text{H}_5\text{O}^2^+\)) and Eigen (\(\text{H}_4\text{O}^2^+\)) cations, respectively, often used to model aqueous hydronic species.

Most of the reactions for the high commercial production in the industrial level is performed in the acidic medium. So, our study has been extended to study the solvation effects during the HER by incorporating the PCM as that for TS1. The energy barrier of the TS2 during the Heyrovsky reaction step to H\(_2\) formation and evolution was found about 8.41 kcal mol\(^{-1}\) in the solvent phase (here H\(_2\)O is solvent used in the calculations) reported in Table 4. This TS2 is also known as Heyrovsky transition state for H\(_2\) evolution.

10. After the formation of the Heyrovsky TS2, the system becomes [WSe\(_2\)]H\(_{\text{Se}}\)\(^{+}\) with the evolution of one H\(_2\) molecule.
and four H$_2$O molecules which is accompanied with an energy cost of –6.27 kcal mol$^{-1}$. This is the place where H$_2$ evolves from the surface of the catalyst and again the reaction process starts from the initial steps either absorbing one electron or releasing the proton as depicted in Figure 4.

Figure 6a,b represents the equilibrium geometry and the schematics representation of the optimized water with hydronium molecular cluster, which consist of three water molecules (3H$_2$O) and one hydronium ion (H$_3$O$^+$). This water hydronium cluster also can be rewritten as four water molecules and a single proton with it (4H$_2$O-H$^+$). The weak H-bonds in the water molecules are highlighted by red dotted ellipse and the weak H–O bond in the hydronium cluster is highlighted by blue dotted ellipse.

As mentioned earlier that the Volmer-Heyrovsky mechanism is the most promising pathway for effective HER in catalysts containing transition metals,[16] so our main emphasis was over the calculation of activation energy barriers for two important saddle points, i.e., transition states i) H$^*$-migration or TS1 and ii) TS2. The changes of energy (ΔE), enthalpy (ΔH), and free energy (ΔG) during different reaction intermediates as well as TSs involved in the HER followed by the Volmer-Heyrovsky reaction pathway in the gas phase calculations are summarized in Table 2.

The present DFT computations found a reaction barrier about ΔG = 2.67 kcal mol$^{-1}$ during the H$^*$-migration reaction or TS1 formation. Similarly, a reaction barrier about 6.24 kcal mol$^{-1}$ has been found during the formation of TS2 in the Heyrovsky reaction process at the W-edges of the pristine 2D monolayer WSe$_2$ material (in gas phase calculation) during HER. This higher value of the Heyrovsky TS2 than the H$^*$-migration TS1 signifies that the Heyrovsky reaction step is the rate-determining step in the Volmer-Heyrovsky reaction mechanism of the HER process in the case of the pristine 2D monolayer WSe$_2$ TMD. A potential energy surface (PES) of this Volmer-Heyrovsky reaction mechanism has been drawn and shown in Figure 7. The variations of Gibbs free energies (ΔG) changes with respect to the proceeding of the reaction steps (i.e., reaction coordinates) involved in the Volmer-Heyrovsky reaction are depicted in Figure 7. As in the commercial field, most of the reactions are carried out in the form of the solution, so a solvent phase calculation of the activation barriers is also necessary to be determined. So, the solvent phase calculation has also been performed by considering the solvent effect of universal solvent “water,” and the respective reaction barriers have been noted down as explained in the above steps of the Volmer-Heyrovsky mechanism.

The present DFT study shows that the activation energy barriers during the H$^*$-migration reaction on the surfaces of the 2D pristine WSe$_2$ material are about 2.67–6.11 kcal mol$^{-1}$ computed in both the gas and solvent phases. Similarly, the activation energy barriers of the H$_2$ formation during the Heyrovsky reaction step are about 6.24–8.41 kcal mol$^{-1}$ in both the gas and solvent phases. These lowest activation energy barriers during H$^*$-migration and H$_2$ formation (in both the gas and solvent phases computations) confirm the better HER catalytic activity of the pristine 2D monolayer WSe$_2$ than other 2D TMDs. It should be mentioned here that its electrocatalytic activity is close enough to the Pt or other noble materials-based electrocatalysts. Figure 8 shows that the pristine 2D monolayer WSe$_2$ material has the lowest activation energy barriers among the previously reported 2D TMDs such as pristine MoS$_2$, WS$_2$ and hybrid W$_x$Mo$_{1-x}$S$_2$ alloys.[9] The lowest activation energy barriers of the 2D monolayer WSe$_2$ (represented by dark green color bar at 12$^{th}$ position of each bar diagram in Figure 8) during the TS (both the transition states TS1 and TS2) formation in both the gas and solvent phases indicate it as an efficient electrocatalyst for HER among other 2D TMDs. A Table S1 is given in the Supporting Information where we compared these reaction barriers with the others 2D TMDs. The electronic energy (E), enthalpy (H), and Gibbs free energy (G) of the (systems, intermediates and TSs) during different reaction steps as well as TSs involved in the HER are summarized in Table S2 in the Supporting Information.

### 3.3.2. Volmer-Tafel Reaction Mechanism

The Volmer-Tafel reaction mechanism is also a two-electron transfer process similar to the Volmer-Heyrovsky reaction mechanism although it is not as complex as the Volmer-Heyrovsky reaction mechanism. In the case of the Volmer-Tafel

![Figure 6](https://www.advancedsciencenews.com/advmatinterfaces.de)
reaction mechanism, two adsorbed adjacent hydrogens on the surface of the catalyst recombine with each other to form H₂ as H⁺ + H⁻→ H₂ and it does not require any further solvated proton like Volmer-Heyrovsky mechanism. The complete reaction processes participating in this proposed reaction pathway are given in Figure 9.

The detailed reaction steps involved in this proposed Volmer-Tafel reaction pathway are described below:

1. This Volmer-Tafel mechanism pathway follows the same route up to the point where the [WSe₂]HWHSe intermediate results from the [WSe₂]HW⁻ intermediate with an energy cost of –9.49 kcal mol⁻¹ with the successive addition of one proton (H⁺) as discussed in the case of Volmer-Heyrovsky mechanism. The complete reaction processes participating in this proposed reaction pathway are given in Figure 9.

2. In the next step, two adsorbed hydrogens (one at the W-site and the other at the Se-site) next to each other combine to form H₂, and this process is known as the Tafel reaction. The reaction phenomena of the H⁺ + H⁻→ H₂ gives to another TS known as the Tafel transition state (TS3), which was computationally found during the HER process. This Tafel TS3 has a single imaginary frequency with an equilibrium W–H bond length 2.21 Å, Se-H bond length 2.45 Å and the final H–H bond length about 0.78 Å. The activation energy barrier of TS3 was found to be 4.56 kcal mol⁻¹ in the gas phase obtained by the same M06-L DFT method. The equilibrium geometry of the TS3 is depicted in Figure 10 along with its schematic representation. The energy barrier of the same TS3 during the Tafel reaction step for H₂ evolution was found about 6.61 kcal mol⁻¹ computed in the solvent phase obtained by the same level of theory.

3. After forming the TS3, the system comes to its initial step [WSe₂] along with the evolution of a single H₂, which is achieved with an energy cost of –15.45 kcal mol⁻¹ and the reaction scheme can be noted by:

\[
[WSe₂]HWHSe → TS3 → [WSe₂] + H₂
\] (12)

The changes in energies during the various steps of the Volmer-Tafel reaction mechanism in the gas phase calculations are reported in Table 3.

In the case of the pristine 2D monolayer WSe₂ TMD, the calculated energy barrier of the H₂ evolution during the Tafel reaction step of the Volmer-Tafel mechanism is much less than the other reported 2D TMDs catalysts. The energy barrier in the Tafel reaction step (i.e., TS3) is also less than the energy barrier of the Heyrovsky reaction step (i.e., TS2) for the H₂ evolution in both the gas and solvent phases calculations. From the gas phase calculation of the Volmer-Tafel reaction pathway of HER, we found a reaction barrier about ΔG = 2.67 kcal mol⁻¹ during the H⁺-migration in the TS1 and a very less reaction barrier about 4.56 kcal mol⁻¹ during the TS3 Tafel reaction step. The values of these barriers are in the range of the DFT accuracy ≈ 4 kcal mol⁻¹.

This higher value of Tafel TS3 compared to the TS1 signifies that the TS3 Tafel reaction step is the rate-determining step in the Volmer-Tafel reaction mechanism of HER when the reaction takes place on the surfaces of the 2D pristine monolayer WSe₂. The relative variations of the Gibbs free energies with respect to the proceeding of the reaction steps involved in the gas phase calculation of the Volmer-Tafel mechanism, i.e., the potential energy surfaces (PESs) are given in Figure 11. Here, the relative changes of Gibbs’ free energy for all the intermediates and TSs are considered with respect to the Gibbs free energy value of the pristine [WSe₂] as the reference value by adopting its energy value as \( G([WSe₂]) - G([WSe₂]) = 0 \) kcal mol⁻¹. All the values of relative free energies (ΔG) are reported in Table 4 and the PES has been drawn with respect to this.
reference value ($G([\text{WSe}_2]) - G([\text{WSe}_2]) = 0 \text{ kcal mol}^{-1}$) as depicted in Figure 11.

In summary, the present DFT study (of the HER on the surfaces of the W$_{10}$Se$_{21}$ non-periodic finite molecular cluster model system of the pristine 2D monolayer WSe$_2$) implies that the activation reaction barrier of the TS3 in the Tafel reaction step is about 4.56–6.61 kcal mol$^{-1}$ in both the gas and solvent phases calculations, respectively. Here, it is noteworthy that the value of the energy barrier ($\Delta G$) of the TS3 appeared in the Tafel reaction step (in the Volmer-Tafel reaction mechanism) is about 1.68–1.80 kcal mol$^{-1}$ less than the barrier of the TS2, i.e., the Heyrovsky transition state in the Volmer-Heyrovsky reaction mechanism computed in both the gas and solvent phases. These values are in the range of the DFT accuracy, and these lower values of the activation energy barriers of the TS1, TS2, and TS3 in the proposed reaction mechanisms indicate that both the pathways have comparable lower energy barriers and both of them can be the assurance pathway for superior HER catalytic performance of the 2D monolayer WSe$_2$ material. These lower reaction barriers signify that the H$_2$ evolution may proceed through any of these pathways with a comparative reaction barrier like the noble metals-based catalysts. The numerical values of the reaction barriers corresponding to different TSs in both reaction pathways are depicted in Table 4 and are graphically presented in Figure 12 to provide a better comparative visualization of the reaction barriers when the HER takes place on the surfaces of the 2D WSe$_2$ TMD.

3.4. Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) Calculations

The HOMO and LUMO calculations have been performed at the equilibrium structures of the transition states to explain the HER process. The role of the atomic orbitals during the formation of TS1 (in the H$^*$-migration reaction step), TS2 and
TS3 (H₂ evolution process during either the Heyrovsky or Tafel reaction steps) can be realized with the visualizations of the HOMO and LUMO calculations of their respective TS structures. The HOMO and LUMO structures of the transition states TS1, TS2 and TS3 are shown in Figure 13. These HOMO and LUMO calculations represent the molecular/atomic orbitals overlapping of multi-electron wavefunction densities. HOMO and LUMO structures of the TS1 during the H•-migration are shown in Figure 13a–d, in which the shifting of the electronic wavefunction density of the H• takes place from the Se site to the W metal atom site. The red color bubble represents the in-phase overlapping of the electron cloud of the 1s orbital of H• atom toward the electron cloud of the 5d orbital of the W atom during the H•-migration reaction at the TS1. The H•-migration in the HOMO and LUMO calculation of the TS1 is highlighted by a black dotted circle, as shown in Figure 13a,d. The energy values of the HOMO and LUMO of the TS1 are $E_{\text{HOMO}} = -7.14 \times 10^{-2}$ eV and $E_{\text{LUMO}} = -6.94 \times 10^{-2}$ eV, respectively, with a HOMO–LUMO gap about $E_{\text{GAP}} = E_{\text{LUMO}} - E_{\text{HOMO}} = 2.00 \times 10^{-3}$ eV corresponding to a photon frequency $4.91 \times 10^{11}$ Hz. The HOMO–LUMO calculation indicates that a wavelength $\lambda = 611.25$ μm is required for the transition of an electron from the HOMO to LUMO. This HOMO–LUMO gap is an important parameter for predicting the stability and the color of the complex in the solution.

Figure 9. Schematic presentation of the proposed two-electron transfer, Volmer-Tafel reaction pathway for HER on the surfaces of the pristine 2D monolayer WSe₂ is shown here.
The HOMO and LUMO structures of the TS2 during the Heyrovsky reaction step of the H₂ evolution are depicted in Figure 13b,e. The formation of H₂ in a steady-state takes place due to stabilization of the system by better atomic orbitals overlapping of the 5d-orbital electron clouds of the W atoms and the 1s-orbital electron clouds of the H₂ molecules as shown in Figure 13b,e. It has been also observed that the electron wavefunction of the 1s-orbital of H• at the W atom overlaps with the H⁺ from the adjacent hydronium ion with water cluster (4H₂O_H⁺) to result an H₂ molecule and is high lightened by a black dotted circle as shown in the HOMO structure of the TS2 in Figure 13b. The energy values of the HOMO and LUMO of the TS2 are about –0.29 eV and –0.25 eV, respectively, with a HOMO–LUMO gap about –0.04 eV. This HOMO-LUMO gap corresponds to a photon frequency of $9.19 \times 10^{12}$ Hz and wavelength of $\lambda = 32.65 \mu$m which is the minimum energy required to transfer an electron from the HOMO to LUMO of TS2. Similarly, Figure 13c–f corresponds to the HOMO and LUMO structures of the Tafel TS3 during the H₂ formation with the recombination and formation of covalent bonding between one H• at the W site and one H• at the Se site during Tafel reaction. The energy level of the HOMO is at –0.20 eV and the energy level of the LUMO is at –0.17 eV resulting in a HOMO-LUMO gap about –0.03 eV in the case of Tafel TS3. The gentle orbital overlapping of molecular orbitals during H•-migration in the Volmer reaction step and H₂ formation in the Heyrovsky and Tafel reaction steps also reveal the excellent catalytic activity of the pristine 2D monolayer WSe₂ for effective HER.

In other words, a better atomic orbital overlap of the s-orbitals of the hydrogen atom attached with the W in the WSe₂ material and the water cluster (3H₂O + H₃O⁺) seemed in the HOMO–LUMO Heyrovsky’s transition state TS2 during H₂ formation has been observed in Figure 13. Similarly, a better atomic orbital overlap of the s-orbitals of the hydrogen atom with the W atom during the H•-migration at the TS1 is shown in Figure 13. These better electron cloud overlap of the atomic orbitals during the H•-migration at the TS1 and the H₂ formation in the Heyrovsky’s/Tafel’s TS2/TS3 have diminished the reaction barrier during the HER process taken place at the surfaces of the 2D WSe₂ TMD. Therefore, it can say that this better stabilization of the atomic orbitals in the reaction rate-limiting

![Figure 10. a) Equilibrium geometry and b) schematic representation of the Tafel transition state TS3 obtained by the M06-L DFT method are shown here.](image-url)

Table 3. Energy changes ($\Delta E$, $\Delta H$ and $\Delta G$) for different intermediates and transition states (TSs) during Volmer-Tafel reaction mechanism are tabulated here. The units are expressed in kcal mol⁻¹.

| Reaction intermediates | $\Delta E$ [in kcal mol⁻¹] | $\Delta H$ [in kcal mol⁻¹] | $\Delta G$ [in kcal mol⁻¹] |
|------------------------|-----------------------------|-----------------------------|-----------------------------|
| WSe₂ → [WSe₂]⁺⁻       | 15.94                       | 16.13                       | 15.38                       |
| [WSe₂]⁺⁻ → [WSe₂]H₅⁺   | –6.18                       | –6.06                       | –6.15                       |
| [WSe₂]H₅⁺ → [WSe₂]H₂S⁺  | 23.11                       | 23.16                       | 24.09                       |
| [WSe₂]H₂S⁺ → H⁺ – migration TS1 | 2.79                 | 2.67                       | 2.67                       |
| H⁺ – migration TS1 → [WSe₂]H⁺⁰ | –15.45                  | –15.53                      | –15.61                      |
| [WSe₂]H⁺⁰ → [WSe₂]H₂H₅⁺   | –9.48                       | –9.31                       | –9.49                       |
| [WSe₂]H₂H₅⁺ → TS3       | 4.59                        | 4.79                        | 4.56                        |
| TS3 → WSe₂              | –8.11                       | –6.57                       | –15.45                      |
step TS2 for H₂-formation is a key for reducing the Heyrovsky’s reaction barrier, thus the overall catalysis indicating a better electrocatalytic performance for H₂ evolution.

3.5. Turnover Frequency (TOF) and Tafel Slope Calculations

To compare the catalytic activities of electrocatalysts, TOF corresponding to the number of H₂ evolved per active site per unit time is another crucial parameter. The higher value of TOF means the better active catalyst, so a catalyst with a higher value of TOF is the need of the concern. Using the transition state theory (TST), the TOF at a specific temperature is given theoretically by:

$$\text{TOF} = \left( \frac{K_B T}{h} \right) e^{-\frac{\Delta G}{RT}} \tag{13}$$

where $K_B$ = Boltzmann constant ($3.298 \times 10^{-27}$ kcal mol$^{-1}$), $T$ = absolute temperature (here it is specified with 298.15 K for our cluster model calculation), $h$ = Planck’s constant ($1.584 \times 10^{-37}$ kcal s), $\Delta G$ = energy barrier and $R$ = universal gas constant ($1.987 \times 10^{-3}$ kcal K$^{-1}$ mol$^{-1}$). Lie et al. computationally found the TOF about $2.1 \times 10^{-5}$ s$^{-1}$ for the pristine 2D MoS₂, $1.5 \times 10^{-3}$ s$^{-1}$ for the pristine 2D monolayer WS₂ in the solvent phase calculations. The highest value of the TOF was about $1.1 \times 10^2$ s$^{-1}$ for the pristine 2D single-layer MoS₂. Lie et al. computationally estimated the TOF value about $1.64 \times 10^{-2}$ s$^{-1}$ corresponding to the molybdenum edge of the pristine 2D single-layer MoS₂. The present DFT study reveals that the value of TOF is about $8.86 \times 10^7$ s$^{-1}$ when the HER takes place at the W edges of the pristine 2D monolayer WSe₂ TMD during the solvent phase reaction in the case of Volmer-Tafel reaction mechanism with an activation energy barrier of 6.61 kcal mol$^{-1}$. Similarly, the value of TOF was found to be $4.24 \times 10^6$ s$^{-1}$ corresponding to the activation energy barrier of 8.41 kcal mol$^{-1}$ (in the solvent phase) during the Heyrovsky reaction at the W-active edges of the pristine 2D monolayer WSe₂ TMD. This ultra-high value of the TOF is much higher (around $3.65 \times 10^4$ times) than the value of TOF of the W₀.₄Mo₀.₆S₂ TMD alloy material during the solvent phase calculation of the Tafel reaction step. This high value of TOF is a significant indicator for the excellent performance of the pristine 2D monolayer WSe₂ for the efficient HER.

The Tafel slope ($b$) shows how efficiently an electrode can produce current in response to change in applied potential. So,
if the Tafel slope (mV per decade) is lower means less overpotential is required to get high current assuming that the reaction rate of the catalyst does not limit with the electron transferred from the support to the catalyst. Theoretically, the Tafel slope (represented by “b”) is given as $b = \frac{RT}{nF}$, where $R =$ universal gas constant, $T =$ temperature in the absolute scale, $F =$ Faraday constant (96 485 C mol$^{-1}$) and $n$ is the number of electrons transferred to the system during the HER process. In other words, it is an equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential. This Tafel slope provides the information regarding the rate-determining step, kinetics, energy required to obtain the required activity, etc., of the electrocatalysts. Tafel slope is an inverse measure of how strongly the reaction rate responds to changes in potential. It is used to evaluate the rate-determining steps during the HER generally assume extreme coverage of the adsorbed species. The preset DFT study has found that the Tafel slope is about 29.583 mV dec$^{-1}$ as $T = 298.15$ K and $n = 2$ (for two electrons transfer) during the evolution of one H$_2$ molecule considering the non-periodic finite molecular cluster model calculations of the 2D WSe$_2$ TMD.

Figure 12. Graphical representation of the reaction barriers for HER on the surfaces of the pristine 2D monolayer WSe$_2$ material is depicted here.

Figure 13. a) HOMO of TS1 during the H$^+$-migration, b) HOMO of TS2 during the Heyrovsky reaction step for H$_2$ evolution, c) HOMO of TS3 during the Tafel reaction step for H$_2$ evolution, d) LUMO of TS1 during the H$^+$-migration, e) LUMO of TS2 during the Heyrovsky reaction step for H$_2$ evolution and f) LUMO of TS3 during the Tafel reaction step of the H$_2$ evolution reaction taken place on the surfaces of the pristine 2D WSe$_2$ TMD material are shown here.
The activation barriers of both the TS2 (Heyrovsky reaction step) and TS3 (Tafel reaction step) during the \( \mathrm{H}_2 \) formation in HER process on the surfaces of various TMDs (like 2D MoS\(_2\), WS\(_2\), W\(_{0.4}\)Mo\(_{0.6}\)S\(_2\) and pristine 2D WSe\(_2\)) are shown in Table 5 and the values of TOFs are shown in Table 5 for assessment. A comparison has been drawn between them about their HER performances considering these activation barriers with the value of TOFs. Tables 4 and 5 shows that the pristine 2D WSe\(_2\) material has the lowest activation barriers during the \( \mathrm{H^*} \)-migration, \( \mathrm{H}_2 \) evolution in the Heyrovsky and Tafel reaction steps with a higher value of TOF compared with other reported 2D TMDs as catalysts. These lower activation energies, higher TOF and lower Tafel slope of the pristine 2D monolayer WSe\(_2\) give an insight into the superior electrocatalytic activity for the efficient HER compared to other reported 2D TMDs.

4. Conclusions

In summary, the equilibrium structure, geometry, and electronic properties (such as band structures, bandgap, Fermi energy level and total DOS) with electrocatalytic performance of the pristine 2D monolayer WSe\(_2\) TMD material have been studied by employing first principles-based hybrid DFT method. The electronic property calculations found that the pristine 2D monolayer WSe\(_2\) is a direct band gap semiconductor with a bandgap about 2.39 eV at the K point in the \( \Gamma-M-K-\Gamma \) high symmetric direction of the irreducible Brillouin zone. A non-periodic finite molecular cluster model system W\(_{0.4}\)Mo\(_{0.6}\)S\(_2\) has been developed to explore the most efficient HER mechanism on the active surfaces of the 2D monolayer WSe\(_2\) material by performing both the possible Volmer-Heyrovsky and Volmer-Tafel reaction pathways at the W-edges (1030). The catalytic performance of the pristine 2D monolayer WSe\(_2\) TMD has been explored by computing the reaction barriers corresponding to the Gibbs free energy change during the \( \mathrm{H^*} \)-migration and \( \mathrm{H}_2 \) evolution on the active surfaces. The present study has found that the reaction barriers of the TS1 and TS2 are about 6.11-8.41 kcal mol\(^{-1}\) in the Volmer-Heyrovsky mechanism during the HER process. The reaction barrier corresponding to the TS3 in the Tafel reaction step of the Volmer-Tafel reaction pathway is about 4.56-6.61 kcal mol\(^{-1}\) in the gas and solvent phases which is lower than the others. These computed single digit values of the activation reaction barriers in both the Volmer-Heyrovsky and Volmer-Tafel mechanisms of the HER process on the surfaces of pristine 2D monolayer WSe\(_2\) TMD is lower than other previously reported 2D TMDs. HOMO–LUMO calculations have been performed at the equilibrium structures of the TSs (TS1, TS2 and TS3, i.e., the TSs formed in the subject reactions; \( \mathrm{H^*} \)-migration and the \( \mathrm{H}_2 \) evolution either in the Heyrovsky reaction step or in the Tafel step) during the HER process. The overlap of the s-orbitals of the hydrogen atom attached with the W in the pristine 2D monolayer WSe\(_2\) TMD and the water cluster (3H\(_2\)O + H\(_2\)O\(^+\)) seemed in the HOMO–LUMO Heyrovsky’s transition state TS2 during \( \mathrm{H}_2 \) formation has been found in the present study, and this better overlap of the atomic orbitals during the \( \mathrm{H}_2 \) creation in the Heyrovsky’s TS2 reduces the reaction barrier. This stabilization of the reaction limiting step in both the gas and solvent phases is for both the \( \mathrm{H^*} \)-migration and Heyrovsky’s reaction energy barriers, which results in a better electrocatalytic performance for HER compared to the ordinary TMDs. This illustrates why the 2D monolayer WSe\(_2\) material has superior HER catalytic activity. The value of TOF was found about \( 4.24 \times 10^6 \) s\(^{-1}\) during the Heyrovsky reaction step, and \( 8.86 \times 10^7 \) s\(^{-1}\) during the Tafel reaction step at the active W-edges. These higher values of TOF confirm the efficient amount of \( \mathrm{H}_2 \) evolution per active site of the pristine 2D monolayer WSe\(_2\) catalysts per unit time. The theoretical value of the Tafel slope was found about 29.58 mV dec\(^{-1}\) during the HER process computed by the DFT method. Therefore, the low values of reaction barriers during adsorbed hydrogen migration and molecular hydrogen formation, low Tafel slope and the ultra-high value of TOF altogether confirm that the pristine 2D monolayer WSe\(_2\) has an excellent electrocatalytic activity for HER. It can be used as a promising and efficient noble metal-free HER catalyst for the efficient production of \( \mathrm{H}_2 \).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
S.P. created the complete design of this current research work on 2D TMDs, and he computationally investigated the equilibrium structures and electronic properties of the pristine 2D monolayer WSe2 material. S.P. explored the whole reaction pathways; transitions states and reactions barriers and he explained the HER mechanism by the DFT calculations. Quantum calculations and theoretical models were designed and performed by S.P. and S.P. wrote the whole manuscript and prepared all the tables and figures in the manuscript. S.P. and V.K. interpreted and analyzed the computed results and S.P. supervised the project work. V.K. revised the manuscript. S.G. helped S.P. to organize the manuscript.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

Keywords
2D TMDs, DFT, electronic properties, HER, Heyrovsky reaction, HOMO and LUMO, Tafel reaction, Tafel slope, TOF, Volmer reaction

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