

Multi-Space Density Functional Simulations of WSe₂ p-n Junctions

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Abstract—Two-dimensional (2D) p-n junctions have attracted growing interest for a wide range of electronic and optoelectronic applications, but their non-equilibrium electronic structure and transport properties have been primarily simulated based on semiclassical approaches that do not incorporate atomistic details of the junction. Here, we combine the multi-space constrained-search density functional theory (MS-DFT) formalism with the simulated doping method to perform first-principles simulations of lateral WSe₂ p-n junctions under finite bias. Based on the nonequilibrium variational minimization procedure, MS-DFT successfully produces an ideal Shockley diode behavior. By resolving bias-dependent Kohn–Sham states, MS-DFT enables direct extraction of spatially varying quasi-Fermi levels (QFLs) across the junction. We find that the QFLs progressively penetrate into the depletion region with increasing forward bias, and that the sharp onset of current density occurs when the QFLs reach the oppositely doped side. Our work uncovers previously undiscussed atomistic features of non-equilibrium 2D p-n junctions and provides guidance for the design of next-generation 2D electronic devices.

Keywords— MS-DFT; simulated doping; 2D p-n junction; WSe₂; quasi-Fermi level;

I. INTRODUCTION

Two-dimensional (2D) materials such as transition metal dichalcogenides (TMDs) and graphene have attracted significant attention owing to the strong impact of reduced dimensionality on their electronic and optoelectronic properties [1]. In particular, laterally aligned 2D p-n junctions are promising building blocks for complementary metal-oxide-semiconductor (CMOS) technology and atomically thin optoelectronics, owing to their atomically homogeneous junction interfaces [2] and the extended depletion widths arising from weak dielectric screening in 2D [3, 4]. Since these features originate from the atomistic nature of 2D materials, an accurate theoretical description of lateral 2D p-n junctions inherently requires an atomic-level treatment.

However, previous theoretical studies of lateral 2D p-n junctions have largely relied on semiclassical charge-sheet models [3, 5], which treat the junction as a continuum and cannot access atomic-level band-edge profiles or quasi-Fermi level (QFL) distributions under non-equilibrium conditions. While first-principles density functional theory (DFT) can in principle resolve these shortcomings, the large computational

cost required to simulate extended lateral junction geometries under finite bias has so far hindered its direct application.

In this work, we combine the multi-space constrained-search DFT (MS-DFT) formalism [6, 7] with the simulated doping method [8] to perform fully atomistic non-equilibrium simulations of lateral WSe₂ p-n junctions (Fig. 1a). The simulated doping method, which corresponds to a special case of the virtual crystal approximation, introduces effective free carriers by modifying the pseudopotentials without explicit dopant atoms (Fig. 1b), and also removes the need for explicit metal electrodes within the MS-DFT framework. Using this combined approach, we extract the spatially resolved QFL profiles at finite bias from the non-equilibrium Kohn-Sham states and their electron occupations, and report the correlation between the QFL profiles and the current flow in the WSe₂ p-n junction.

II. METHOD

All DFT and MS-DFT calculations were carried out using the SIESTA package [9] within the local density approximation (LDA) [10]. The atomic cores were described by Troullier-Martins norm-conserving pseudopotentials [11], and double- ζ -plus-polarization basis sets together with an 80 Ry real-space mesh cutoff were used. A k-point mesh of $8 \times 1 \times 1$ was adopted for the lateral WSe₂ p-n junction, and the simulation cell was extended to 48 nm along the out-of-plane direction to capture the long-range electrostatic interactions inherent to 2D junctions.

To apply n- and p-type doping in the WSe₂ layer, we employ the simulated doping method [8], in which the nuclear and valence electron charges of the W and Se atoms are modified by a small fractional amount (e.g., $Z = 74 + 0.003$ for n-type W). This scheme only weakly perturbs the underlying pseudopotentials but effectively shifts the Fermi level of WSe₂ in accordance with the intended doping type while preserving its pristine band structure (Fig. 1b and Fig. 1c).

From the non-equilibrium electronic structures obtained by MS-DFT, the electron transmission and current density were evaluated within the matrix Green's function (MGF) formalism under the Landauer-Büttiker picture [12]. The electron transmission is given by

$$T(E; V_b) = \text{Tr}[\Gamma_L(E; V_b)G(E; V_b)\Gamma_R(E; V_b)G^\dagger(E; V_b)], \quad (1)$$

where G is the retarded Green's function for the channel C , and $\Gamma_{L/R} = i(\Sigma_{L/R} - \Sigma_{L/R}^\dagger)$ are the broadening matrices. The current density-bias voltage ($J - V_b$) characteristics were then obtained from the Landauer-Büttiker formula,

$$I(V_b) = \frac{2e}{h} \int T(E; V_b) [f(E - \mu_R) - f(E - \mu_L)] dE, \quad (2)$$

The spatially resolved QFL profiles were reconstructed from the bias-dependent Kohn-Sham (KS) states: at each energy, the x - y plane-projected KS wavefunction is color-coded by its MS-DFT electron occupation factor, following the procedure detailed in our earlier work [6].

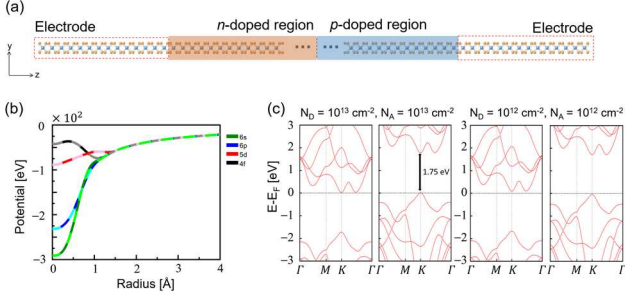


Fig. 1. Atomic structure of (a) the lateral WSe₂ p-n junction. (b) Pseudopotentials of the pristine (solid lines) and p-doped (dashed lines) W atom. (c) Electronic band structures of the doped WSe₂ (left two panel, $N_D = 10^{13} \text{ cm}^{-2}$, $N_A = 10^{13} \text{ cm}^{-2}$, right two panel, $N_D = 10^{12} \text{ cm}^{-2}$, $N_A = 10^{12} \text{ cm}^{-2}$)

III. RESULTS AND DISCUSSION

A. Symmetric & Asymmetric WSe₂ p-n junction

As the first step, we introduce fractionally charged W and Se atoms, which enable n- and p-type doping in the WSe₂ layer. Applying the simulated doping method to monolayer WSe₂ by modifying both the W and Se atoms, we observe that the Fermi level (E_F) of WSe₂ shifts according to the doping type while preserving its original band structure (Fig. 1c).

We then carry out equilibrium DFT calculations for the lateral 2D WSe₂ p-n junction. Fig. 2a (top panel) shows the spatially resolved density of states (DOS) for the highly doped symmetric WSe₂ p-n junction ($N_D = N_A = 10^{13} \text{ cm}^{-2}$) at $V_b = 0 \text{ V}$. Given that the E_F difference between the n- and p-type WSe₂ layers is 1.74 eV, we confirm that the expected built-in potential is well recovered at $V_b = 0 \text{ V}$. The spatially resolved DOS (Fig. 2a, top panel) directly resolves the atomic-scale bending of the conduction- and valence-band edges across the junction, from which the built-in potential is read off — information inaccessible to charge-sheet models. The corresponding charge density difference (Fig. 2a, second panel) develops long tails that decay slowly away from the junction, so that full depletion does not occur even for this abrupt junction, reflecting the weak out-of-plane dielectric screening characteristic of 2D materials.

From the macroscopically smoothed Hartree potential profile (Fig. 2a, bottom panel), we define the depletion width as the distance between x_n and x_p , where x_n (x_p) is the position at which the electric field in the n-doped (p-doped) WSe₂ region becomes smaller than $0.0005 \text{ eV/\AA}$. We thereby obtain a depletion width of 12 nm ($x_n = 6 \text{ nm}$, $x_p = 6 \text{ nm}$) for the symmetric WSe₂ p-n junction at $V_b = 0 \text{ V}$. This depletion width is several times larger than that of a bulk p-n junction at comparable doping, a direct consequence of the long-range, weakly screened electrostatics of the 2D junction [3, 4].

Adopting the MS-DFT formalism, which enables non-equilibrium calculations, we next obtain the electronic structure of the symmetric WSe₂ p-n junction ($N_D = N_A = 10^{13}$

cm^{-2}) at $V_b = 1 \text{ V}$ (Fig. 2b). From the spatially resolved DOS (Fig. 2b, top panel), we identify a contact potential of 0.74 eV, confirming that MS-DFT correctly describes the non-equilibrium conditions of the 2D p-n junction within a first-principles approach. This is further supported by the charge density difference (Fig. 2b, second panel) and the macroscopically smoothed Hartree potential (Fig. 2b, bottom panel). As the bias increases to 1 V, the magnitude of charge density is reduced owing to majority-carrier injection from the quasi-neutral regions. As a result, the depletion width obtained from the macroscopically smoothed Hartree potential (Fig. 2b, bottom panel) decreases to 8.4 nm ($x_n = 4.1 \text{ nm}$, $x_p = 4.3 \text{ nm}$). We find that the resulting depletion width scales approximately as the square root of the contact-potential difference across the bias range studied, which can be traced to the charge density varying nearly linearly within $\sim 2 \text{ nm}$ of the junction interface rather than forming an abrupt interfacial dipole.

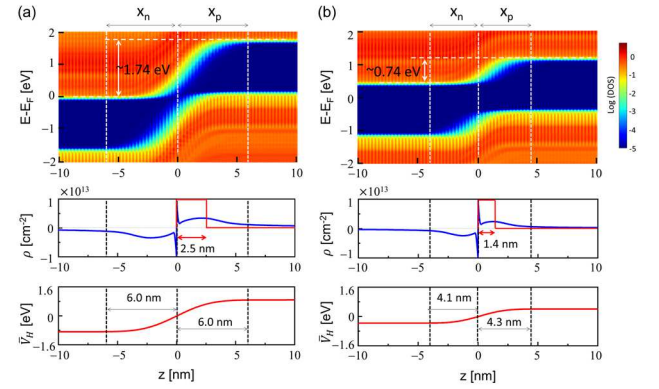


Fig. 2. Symmetric 2D WSe₂ p-n junction ($N_D = 10^{13} \text{ cm}^{-2}$ and $N_A = 10^{13} \text{ cm}^{-2}$) (a) Spatially-resolved DOS at $V_b = 0 \text{ V}$ (top panel), the space charge density (second panel), and the macroscopically smoothed Hartree potential profiles in the WSe₂ layer (bottom panel). Here, the left side WSe₂ layer is n-doped and the right side WSe₂ layer is p-doped. In the space charge density, the blue and red solid lines are obtained from DFT and analytic equation, respectively. (b) Spatially-resolved DOS at $V_b = 1 \text{ V}$ (top panel), the space charge density (second top panel), and the macroscopically smoothed Hartree potential profiles in the WSe₂ layer (bottom panel).

Given that asymmetric doping conditions are prevalent in experimental situations, we next consider an asymmetric WSe₂ p-n junction ($N_D = 10^{13} \text{ cm}^{-2}$ and $N_A = 10^{12} \text{ cm}^{-2}$) (Fig. 3a-b). In the spatially resolved DOS at $V_b = 0 \text{ V}$ (Fig. 3a, top panel), most of the band bending occurs on the lightly doped p-doped side, which recovers the expected built-in potential of $\sim 1.68 \text{ eV}$. The corresponding charge density (Fig. 3a, second panel) and macroscopically smoothed Hartree potential (Fig. 3a, bottom panel) likewise develop markedly asymmetric profiles, so that the depletion width extends predominantly into the p-doped WSe₂ region. While the DFT depletion width on the p-doped side ($x_p = 20.1 \text{ nm}$) is close to the value from the analytic equation ($x_p = 23.1 \text{ nm}$), closer inspection of the space charge density reveals a substantial discrepancy between them: we observe an inverted space charge density (hole accumulation) at the junction interface on the p-doped side, arising from holes expelled from the heavily n-doped region. This effect is not captured by the classical charge-balance relation $x_p/x_n = N_A/N_D$, which predicts $x_p/x_n = 10$, whereas our DFT calculation gives $x_p/x_n = 5.9$ due to this inverted charge distribution on the p-doped side.

We then apply a finite bias to the asymmetric junction within the MS-DFT formalism. As V_b increases to 1 V, the contact potential is reduced from $\sim 1.68 \text{ eV}$ to $\sim 0.68 \text{ eV}$ (Fig. 3a-b, top panels) and the electric field in the vacuum region weakens accordingly, reducing the overall depletion width

(Fig. 3a-b, bottom panels). Notably, owing to the strong doping asymmetry, this reduction is highly asymmetric between the two sides: the depletion width on the heavily doped n-doped side ($x_n \approx 3.5$ nm) remains essentially unchanged with bias, whereas the depletion width on the lightly doped p-doped side decreases substantially, from $x_p = 20.1$ nm at $V_b = 0$ V to $x_p = 11.8$ nm at $V_b = 1$ V, indicating that the response of the junction to forward bias is governed predominantly by the more lightly doped side.

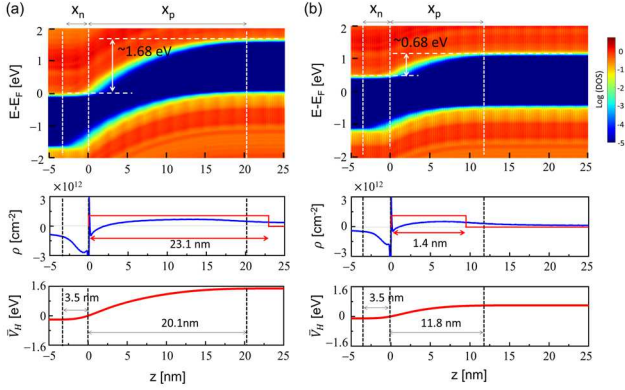


Fig. 3. Asymmetric 2D WSe₂ p-n junction ($N_D = 10^{13}$ cm⁻² and $N_A = 10^{12}$ cm⁻²) (a) Spatially-resolved DOS at $V_b = 0$ V (top panel), the space charge density (second panel), and the macroscopically smoothed Hartree potential profiles in the WSe₂ layer (bottom panel). Here, the left side WSe₂ layer is n-doped and the right side WSe₂ layer is p-doped. In the space charge density, the blue and red solid lines are obtained from DFT and analytic equation, respectively. (b) Spatially-resolved DOS at $V_b = 1$ V (top panel), the space charge density (second top panel), and the macroscopically smoothed Hartree potential profiles in the WSe₂ layer (bottom panel).

B. Quasi-Fermi level profiles in the WSe₂ p-n junction

We now explore the current density-voltage (J - V_b) characteristics and their correlation with the non-equilibrium QFL profiles of the symmetric WSe₂ p-n junction ($N_D = N_A = 10^{13}$ cm⁻²) in Fig. 4. From the $J - V_b$ curve (Fig. 4a), we find that the knee voltage is 1.4 V. Since our formalism does not include recombination and generation currents, fitting the log-scale J - V_b curve (inset of Fig. 4a) to the Shockley equation yields an ideality factor $\eta \approx 1$, consistent with ideal diode transport. To further validate this, we compare the MS-DFT $J - V_b$ curve with the analytic ideal-diode equation for the diffusion current in a p - n junction [13],

$$J_{ideal} = J_p + J_n = J_0 \left[\exp\left(\frac{qV_b}{\eta k_B T}\right) - 1 \right], \quad (3)$$

where $J_0 = q \left[\frac{D_p}{L_p} p_n + \frac{D_n}{L_n} n_p \right]$ is the saturation current density, p_n (n_p) is the minority hole (electron) density in the n-doped (p-doped) region, and $D_{n(p)}$, $L_{n(p)}$ are the corresponding diffusion coefficients and lengths. The minority carrier densities are extracted from our DFT calculations, while the carrier mobilities and intrinsic carrier density of WSe₂ are taken from [3], and the carrier lifetimes from [14]. In the forward-bias regime, the MS-DFT current closely follows this analytic prediction with $\eta = 1$, confirming that the atomistic calculation correctly captures the ideal drift-diffusion transport mechanism. This ideal diffusion-like behavior can be attributed to the smoothly bent Hartree potential and corresponding band edges across the depletion region (Fig. 2b), which permit elastic dephasing transport without invoking artificial scattering probes.

We then extract the QFL profile at $V_b = 1.0$ V (Fig. 4b) and examine how it relates to the current flow through the junction. Before the main discussion, we note that the QFLs extracted from the first-principles approach have a

momentum-space (k -space) dependence; therefore, many QFLs exist with respect to the k -space. This momentum-resolved structure of the QFLs is a feature accessible only within the first-principles approach, in contrast to the single pair of QFLs assumed in classical descriptions of p - n junction phenomena such as Shockley-Read-Hall (SRH) recombination [3].

While many QFLs exist depending on the k -space, here we consider only the QFLs extracted from the special k -point that mainly carries the current within the bias window (the QFLs of the other k -points are not shown). At a forward bias of $V_b = +1$ V, we find that the QFLs originating from the n-doped (p-doped) WSe₂ are pulled upward (downward) and no longer overlap in energy, so that no electron transmission appears around the bias window (Fig. 4b, right panel). This direct correspondence between the QFL spatial profiles and the current flow provides an atomistic picture of non-equilibrium transport in lateral 2D p - n junctions that is inaccessible to semiclassical models.

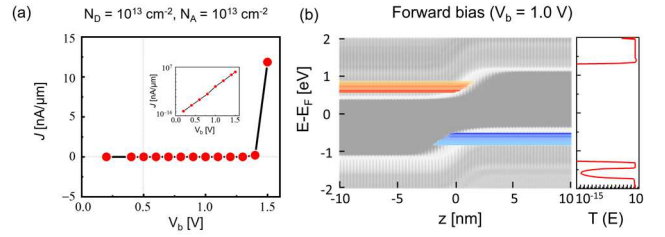


Fig. 4. (a) $J - V_b$ curve of the symmetric WSe₂ p-n junction ($N_D = 10^{13}$ cm⁻² and $N_A = 10^{13}$ cm⁻²). Inset curve in (a) represents the logscale $J - V_b$ curve. The QFL profiles (left panel) and corresponding electron transmissions (right panel) at (b) $V_b = 1.0$ V.

IV. CONCLUSION

We have demonstrated a first-principles framework for the non-equilibrium simulation of lateral WSe₂ p-n junctions, obtained by combining the simulated doping scheme with the MS-DFT formalism. At equilibrium, the approach reproduces the junction electrostatics directly from the atomistic electronic structure, recovering the built-in potential and the extended depletion width that arises from the weak dielectric screening of 2D materials—both extracted from the spatially resolved density of states rather than assumed, as in semiclassical charge-sheet models.

Under finite bias, the framework reproduces an ideal Shockley diode response ($\eta \approx 1$) and, by resolving the bias-dependent Kohn–Sham states, gives access to the spatially varying quasi-Fermi levels (QFLs) across the junction. We find that the sharp onset of the current density coincides with the QFLs penetrating into the oppositely doped region, providing a direct atomistic criterion for the turn-on of 2D p - n junctions that goes beyond the single pair of QFLs assumed in conventional descriptions. Building on these results, the framework extends naturally to more general doping profiles and 2D heterojunctions, offering a predictive atomic-scale platform for the design of next-generation 2D devices such as tunnel FETs, photodetectors, and 2D-CMOS elements.

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