# Exciton physics in transition-metal dichalcogenides at the atomic scale

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**Abstract:** We present an atomistic model for excitons in monolayer transition-metal dichalcogenides consistent with recent experiments. Using this model we show how to extend exciton lifetimes, which could be important for future optoelectronic applications.

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## 1. Introduction

Monolayer transition metal dichalcogenides (TMDs) are two-dimensional semiconductors with direct bandgaps in the visible range. The light absorption spectrum contains two main characteristic features “A” and “B” [1], whose energy separation are related to the sizable spin-orbit coupling in these materials. These features are widely believed to reflect excitonic states inside the band gap. As there is no obvious feature related to be band gap, recently reported exciton binding energies span a wide range up to 1 eV [2–5], suggesting that the dielectric screening in these 2D materials is relatively poor. With the electron and hole concomitantly bound tightly, lattice effects should be considered. Understanding the excitons at the atomic scale is therefore important for this reemerging area.

Herein, we present an atomistic model of exciton states in TMDs within a tight-binding framework. The model relies only on physical quantities that have all been determined, except for the dielectric constant, which remains unclear. By varying the dielectric constant, we show the importance of the lattice for strongly bound excitons. A Lorentz-Drude-Gaussian permittivity model [6] is then used to capture broadening in the absorption spectrum. Lastly, we show that the lattice breaks the subshell degeneracy in the exciton spectrum predicted by the 2D hydrogen model and allows exciton population to be shifted into dark states to extend exciton lifetimes [7].

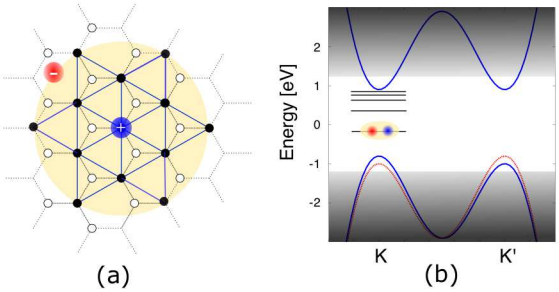


Fig. 1. (a) The presented atomistic model for excitons in TMDs adopts a triangular-tiled structure centered on transition-metal sites (black circles). (b) Sub-bandgap exciton states sit at the K-point valleys of the electronic band structure.

## 2. Model description

Bearing semblance to the hydrogen-model Hamiltonian [8], the atomistic-model Hamiltonian consists of an electron Hamiltonian $H_e$, a hole Hamiltonian $H_h$, and an attractive Coulomb potential $V$. Because the conduction and valence band states are predominantly $d$-orbitals on the transition metal sites, we adopt the triangular-tiled crystal structure shown in Fig. 1a to discretize the atomistic Hamiltonian. In absence of orbital hybridization, the atomistic model provides a suitable approximation of the electronic bands within a few-hundred meV of the band edges. Hence, we restrict the model to optical transitions in the K(K′) valleys, as Fig. 1b illustrates.

The nearest-neighbor hopping parameter for the triangular-tiled structure in Fig. 1a is

$$t_{j,j'} \equiv \frac{4\mathrm{Ry}}{3m}\left(\frac{a_0}{a_l}\right)^2 + i\frac{\Delta E_{SO}}{9} sin\left[4\pi\frac{(x_j - x_{j'})}{3\,a_l}\right], \tag{1}$$

where $\Delta E_{SO}$ describes the valence band split at the K(K′) valleys, $x_j$ is the position along the direction one of the lattice vectors, $m$ is the reduced effective mass in units of the electron mass $m_0$, Ry is the Rydberg energy, $a_0$ is the Bohr radius, and $a_l$ is the lattice constant. The expression for the Coulomb potential for $j \neq 0$ is $V_j = 2a_0\mathrm{Ry}/\varepsilon_r r_j$, where $\varepsilon_r$ is the dielectric constant and $r_j$ represents the relative position of the oppositely charged particles. We determine empirically $V_0$, the potential for $j = 0$, by matching the exciton binding energy of the atomistic model to the hydrogen model at $\varepsilon_r = 10$. At this relatively large dielectric constant, we assume the hydrogen model gives a reasonable prediction of the exciton binding energy as the excitons then span many lattice sites.

## 3. Tightly bound exciton states

Fig. 2a shows model binding energies for the most strongly bound exciton states in monolayer molybdenum disulfide ($MoS_2$) as a function of the dielectric constant. The atomistic model deviates from the the hydrogen model when electron/hole separations are on the atomic scale. The approximate radial expectation value for both molybdenum disulfide $MoS_2$ and molybdenum diselenide $MoSe_2$ ground state excitons is approximately $0.8\,\varepsilon_r$ [Å]. As $\varepsilon_r$ approaches unity, the exciton's expected radius becomes shorter than the lattice constant $\sim 3$Å, making lattice effects important. One example is the binding energy in Fig. 2a. Below a dielectric constant of about $\varepsilon_r = 7$, the 2D hydrogen model and atomistic model noticeably deviate from one another. Within the presented range of dielectric constants in Fig. 2a, the binding energies of the atomistic model agree reasonably with a related experiment [2] on $MoS_2$. Furthermore, the atomistic model automatically predicts both the "A" and "B" peaks. The latter is included ad-hoc in the hydrogen model.

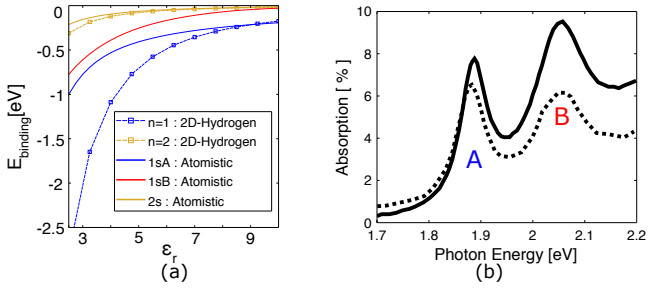


Fig. 2. (a) $MoS_2$ exciton states plotted versus dielectric constant. (b) LDG model broadens "A" and "B" absorption peaks for suspended (solid line) and supported (dash line) $MoS_2$.

In Fig. 2b, a Lorentz-Drude-Gaussian (LDG) permittivity model [6] captures broadened features in the $MoS_2$ absorption spectrum. A frequency-dependent dielectric response to an applied field is represented by a sum of Lorentzian and Gaussian functions at resonant exciton energies outputted from the atomistic model.

## 4. Lifted Degeneracy

Dark exciton states are often overlooked because they are optically inactive and usually inaccessible, but if excited to, an exciton in a dark state has a significantly longer lifetime compared to an exciton in a bright state [7]. Fig. 3a shows a lifted degeneracy of approximately 70 eV when $\varepsilon_r = 3$ between $2s$ and $2p$ states for $MoS_2$ and $MoSe_2$. The energy

separation between these states increases with a decreasing dielectric constant. This sizable energy separation is in the near- to mid-IR range. With an intrinsic optical-phonon energy around 30 meV [9], the energy separation between the $2s$-state and $2p$-state is wide enough to mitigate optical-phonon-induced scattering.

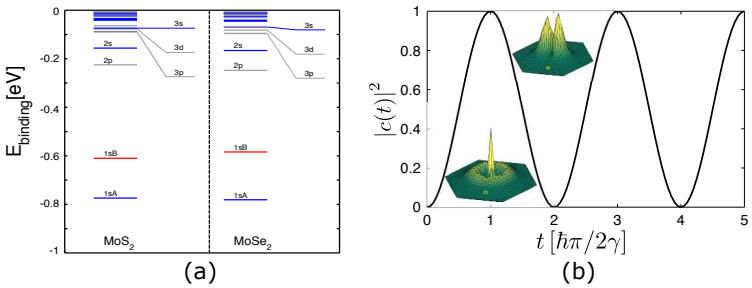


Fig. 3. (a) At $\varepsilon_r = 3$, bright-states (blue and red lines) and dark-states (grey lines) are non-degenerate. (b) Exciton population oscillating between bright-$2s$ and dark-$2p$ states at the Rabi frequency, $\gamma/\hbar$.

An optical transition between the $2s$ and the $2p$ exciton is dipole-allowed under the azimuthal condition, $\Delta l = \pm 1$. A mid-IR laser tuned to resonance with the $2s$-to-$2p$ transition energy oscillates the exciton between these states, as shown in Fig. 3b. The time $\tau$ needed to shift the exciton population to the dark-$2p$ state depends on the two-state electronic coupling term $\gamma$, which in turn is dependent on the electric field component of the laser. Within the time frame of a given laser pulse duration, the population or absorption cycle of the dark state occurs in multiples of $\hbar\pi/2\gamma$.

## 5. Conclusion

In conclusion, we have presented a model for exciton states in TMDs on the atomic scale and how it can be used in conjunction with a frequency-dependent permittivity model to capture the broadening in the absorption spectrum at the exciton peak energies. Lastly, we have presented the Rabi frequency for an exciton to transition into a dark $2p$-state to extend its life time. This work has been funded by the Office of Naval Research (ONR), directly and through the Naval Research Laboratory (NRL). F.T. and E.S. acknowledge support from NRL through the NRC Research Associateship Program and the ONR Summer Faculty Program, respectively.

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