Theory and Applications of Strongly Bound Excitons in Layered Transition-Metal Dichalcogenides

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***Abstract*—A minimalistic exciton model is developed to describe the excitons in pristine semiconducting crystals. The model accounts for the lattice, spin-orbit, and exchange interactions, and hence describes how excitons interact with electrons and photons.**

I. Introduction

Monolayers of transitional metal dichalcogenides (TMDCs) are atomically thin materials with potential applications in optoelectronics and valleytronics due to their direct band-gap, semiconducting, and highly dispersive nature [1]–[4]. The weak screening in monolayer TMDCs makes it a necessity to treat the electron and hole separation in the strongest bound excitons at the atomic scale. In this presentation, we first present a minimalistic exciton model that accounts for the lattice and the spin-orbit and exchange interactions, thus making this model appropriate across the spectrum from Wannier to Frenkel excitons. In the second part, we describe how this model can be used to describe the interaction of excitons with electrons and photons for the accurate modeling of opto-electronic devices loaded with monolayer TMDCs. In the third and final part, we show that the exciton lifetimes could be extended by transitioning the excitons into excitonic dark states. Longer exciton lifetimes could make these materials candidates for applications in energy management and quantum information processing.

A. An Atomistic Model for Excitons in Monolayer TMDCs

Due to a weak dielectric screening in layered TMDCs, strongly bound excitons have binding energies up to at least several hundred meV's. Traditionally excitons are treated as hydrogen-like quasi-particles but we recently show that the hydrogen model breaks down for these experimentally observed strongly bound, room-temperature excitons [3]. To capture these non-hydrogen-like photo-excitations, an atomistic model is introduced as an alternative model to computationally expensive calculations.

We solve the Schrödinger equation, $\hat{H}\psi_{nl} = E_{nl}\psi_{nl}$, to calculate exciton wavefunctions (ψ_{nl}) and eigenenergies (E_{nl}) of a TMD layer by employing an appropriate Hamiltonian, $\hat{H}$, where $n = 1, 2, \cdots$ and $l = 0, \cdots, n-1$ are the quantum numbers corresponding to $1s$, $2s$, $2p$, etc. states. Exciton envelope functions on the transition metal sites can be expanded in terms of Wannier functions, i.e. $\phi(\vec{r} - \vec{R}_j) \equiv \langle \vec{r} | \phi_j \rangle$, where j is the position index of the electron in the conduction band relative to the hole in the valence band, or vice versa, so that $\psi_{nl} = \sum_j c_j \phi(\vec{r} - \vec{R}_j)$. The Hamiltonian, which represents single-particle contributions, the nonlocal Coulomb interaction, and the direct - exchange interaction difference, can be written as

$$\hat{H} = \sum_{\langle j,j' \rangle} t_{j,j'} \left|\phi_j\right\rangle \left\langle\phi_{j'}\right| - \sum_{j \neq 0} V_j \left|\phi_j\right\rangle \left\langle\phi_j\right| - V_1 \left|\phi_0\right\rangle \left\langle\phi_0\right|, \quad (1)$$

where $V_j = 2a_0 \mathrm{Ry}/\epsilon_r r_j$, ϵ_r is the in-plane permittivity of TMD, a_0 is Bohr radius, r_j is the distance of the j^{th} site with respect to origin, Ry is the Rydberg energy, and the effective hopping parameter is

$$t_{j,j'} = \frac{2\mathrm{Ry} m_0 a_0^2}{3 m a_l^2} + i \frac{E_{SO}}{9} \sin\left(4\pi \frac{(x_j - x_{j'})}{3a_l}\right), \quad (2)$$

which is a function of the valence band split, E_{SO}. Above, x_j is the position along the direction of one of the lattice vectors, m_0 is mass of an electron, m is reduced mass, and a_l is lattice constant. The model predicts both bright excitons and dark excitons, and their broken degeneracy in monolayer TMDCs. For strongly bound exciton states, the lattice potential significantly distorts the envelope wave functions, which affects the predicted exciton peak energies.

B. A Lorentz-Drude-Gaussian Permittivity Model

The bright states obtained with the atomistic model are used as the resonance frequencies of a hybrid Lorentz-Drude-Gaussian permittivity model for MoS_2 [4], in which oscillation strengths and damping coefficients are obtained from the experimental results for the differential transmission and reflection spectra of monolayer MoS_2 coated quartz and silicon substrates, respectively. All the parameters used in the permittivity model are functions of Fermi energy and temperature.

The Lorentz-Drude part of the frequency dependent permittivity is given by

$$\epsilon_c^{LD}(\omega) = \epsilon_\infty + \sum_{j=0}^{5} \frac{a_j \omega_P^2}{\omega_j^2 - \omega^2 - i\omega b_j} \quad (3)$$

where ω_P is the plasma frequency, ϵ_∞ is DC permittivity, ω_j's, a_j's and b_j's are resonance frequency, oscillator strength, and damping coefficients, respectively, for the j^{th} oscillator. Basically, resonance frequencies are the ω values where we observe absorption peaks. In our experiments, they are found to be at 1.88 eV, 2.03 eV, 2.78 eV, and 2.91 eV, which agree well with the other experimental [2] and theoretical [1] studies. Herein, we adopt an atomistic model with the in-plane permittivity $\epsilon_r^{\parallel} = 2.5$ and onsite $e-h$ interaction fitted to give

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resonance energies close to the observed peaks at 1.92, 2.08, 2.8, and 2.94 at $T = 0$ K. The other parameters used for the solution are lattice constant, $a_{lattice} = 0.316$ nm, valence band split, $E_{SO} = 0.152$ eV, and reduced mass $m = 0.32m_e$, where m_e is the mass of an electron. Considering the standard semiconductor bandgap temperature dependency, our experimental results obtained at room temperature are in good agreement with the theoretical results (roughly they are all 0.03-0.05 eV less than the theoretical results valid for $T = 0$ K). However the tail around 4 eV suggests another resonant frequency in the $\hbar\omega > 4$ eV region, which also appears in the experimental results. We assume this fifth resonant occurs at 4.34 eV.

For the Gaussian component, we first define the imaginary part as

$$\epsilon_i^G(\omega) = \alpha \exp\left(-\frac{(\hbar\omega - \mu)^2}{2\sigma^2}\right), \tag{4}$$

which is a typical Gaussian distribution function with a mean of μ, variance of σ, and maximum value of α. Then we calculate the real part using Kramers-Kronig relation

$$\epsilon_r^G(\omega) = -\frac{1}{\pi}\mathrm{PV}\int_{-\infty}^{\infty}\frac{\epsilon_i^G(\omega')}{\omega' - \omega}d\omega'. \tag{5}$$

Using the experimentally measured plasma frequency of 28.3 meV, in a non-linear least squares method, we find the optimum values for the unknown parameters in Eqs (3) and (4) as follows: $\epsilon_\infty = 4.44$, $\alpha = 23.224$, $\mu = 2.7723$, $\sigma = 0.3089$, and a_j, b_j, ω_j values are listed in Table I. Gaussian component act like a carrier of the main behavior we observe in the absorption spectra and each LD oscillator corresponds to absorption peaks.

TABLE I. OSCILLATION STRENGTH, DAMPING COEFFICIENT, AND RESONANCE FREQUENCIES FOR THE LORENTZ-DRUDE OSCILLATORS USED IN (3). ALL COEFFICIENTS ARE NORMALIZED WITH $\hbar$.

j	$a_j/\hbar$	$b_j/\hbar$	$\omega_j/\hbar$
0	2.0089×10^5	1.0853×10^{-2}	0
1	5.7534×10^4	5.9099×10^{-2}	1.88
2	8.1496×10^4	1.1302×10^{-1}	2.03
3	8.2293×10^4	1.1957×10^{-1}	2.78
4	3.3130×10^5	2.8322×10^{-1}	2.91
5	4.3906×10^6	7.8515×10^{-1}	4.31

By subtraction Fermi energy from the spin-orbit coupling energy, the atomistic model becomes gate voltage dependent. Moreover, if we implement the temperature dependency model proposed in [5], the atomistic model can estimate the eigenenergies as functions of gate voltage and temperature.

C. Using Dark States for Exciton Storage

Lastly, we propose the use of excitonic dark states to extend exciton lifetimes in TMDCs as follows. The scattering rate between bright and dark states depends on the energy separation between these states. The subshell degeneracy of TMDCs and having energy separation the dark $2p$ and the bright $2s$ states above the thermal energy at room temperature make them excellent materials to limit spontaneous scattering. Using two lasers (one for exciton population in the bright s-states and another one for moving that population into the $2p$ states), we can control the release of the excitation energy.

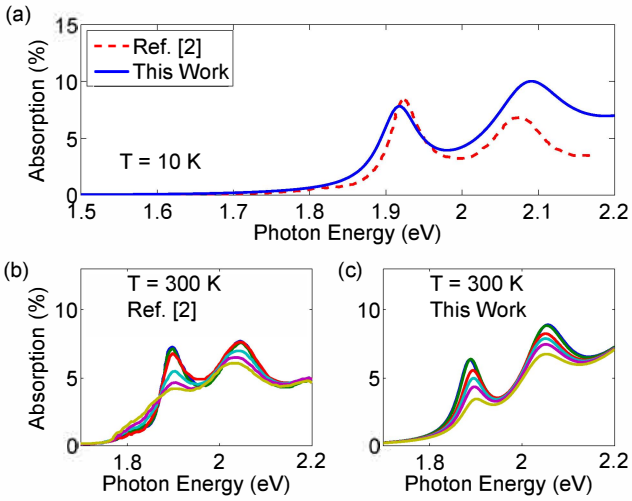

Fig. 1. Absorption spectrum of MoS_2 at $T = 10$ K (top) and $T = 300$ K. In (a), $V_g = -107$ V, corresponds to the undopped case, i.e. $E_F = 0$ eV [2]. In (b) and (c), gate voltage values are $V_g = (-70, -40, 10, 30, 50, 80)$ V. As V_g is increased, the absorption decreases (from blue to yellow lines).

At the conference, we will discuss our theoretical approach for calculating the exciton population and the needed transition matrix elements that involce exciton states obtained from our atomistic exciton model. Numerical results and comparisons will be provided.

II. CONCLUSION

New theoretical frameworks are developed to describe the excitonic properties of TMDCs and their interactions with electrons and photons. Extending exciton lifetimes using excitonic dark states could lead to future applications from energy storage to quantum-based information processing.

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