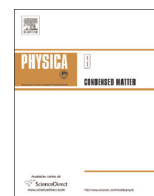




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Excitonic polarons in low-dimensional transition metal dichalcogenides

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ABSTRACT

We examine the excitonic polaron properties of common monolayer transition metal dichalcogenides (MoS₂, MoSe₂, WS₂ and WSe₂). The excitonic polaron is formed when excitons interact with acoustic or optical phonons via coupling to the deformation potentials associated with the conduction and valence bands. A unitary transformation which performs an approximate diagonalization of the exciton–phonon operator is used to evaluate the ground state energy of the excitonic polaron. We derive analytical expressions of the changes in the excitonic polaron energy and mass at small exciton wavevectors involving the deformation potential due to optical phonons. The polaronic effect of the monolayer transition metal dichalcogenides is examined by comparing changes in the energy gap shift and effective masses based on known deformation potential constants for carrier–phonon interactions. Our results indicate the occurrence of comparable energy shifts when the ground state exciton interacts with optical or acoustic phonons. We extend our calculations to explore the influence of exciton–lattice interactions on the binding energies and the self-trapping of excitons in two-dimensional layers of transition metal dichalcogenides.

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1. Introduction

Low-dimensional layered transition metal dichalcogenides are currently studied with increased interest due to their versatile electronic properties [1–7] and potential use in a wide range of chemical and physical systems [8–12]. In transition metal dichalcogenides MX₂, the intra-layers of the M metal plane (M=Mo, W, Nb) are held between the chalcogen X, (X=S, Se) atomic planes by covalent bonding. The inter-layers held together by weak van der Waals forces can be separated into distinct layers, hence it is possible to fabricate materials with just a few atomic layers with ease using exfoliation techniques [13,14]. The monolayer is represented by the hexagonally ordered plane of metal atoms sandwiched between two other hexagon planes of chalcogen atoms. This configuration enables control of opto-electronic properties which are determined by the actual number of layers making up the metal dichalcogenide sample. For the well known Molybdenum disulfide (MoS₂) [15], the indirect-to-direct transition in its electronic band gap translates to a notable enhancement in the photoluminescence spectral peaks [3,16].

Excitons with large binding energies dominate the optical spectra of the low dimensional metal chalcogenides as demonstrated in recent experimental works and theoretical works

involving the prototypical MoS₂ [3,16,4,5,17–19]. Exciton–phonon interactions, in particular, play an important role in the optical and intrinsic transport properties of material systems. The exciton effective mass and energy undergo shifts which are dependent on the strength of the exciton–phonon coupling. The exciton and its accompanying lattice distortion can be conceptualized as a dressed particle or excitonic polaron, with a self-energy and a re-normalized mass. The formation of a composite excitonic polaron has been examined in material systems of various configurations [29,20–28]. However the excitonic polaron remains to be explored in new configurations of low dimensional transition metal chalcogenides. Due to the layered structures of metal chalcogenides, a variety of phonon modes that interact via short range and long forces arise giving rise to a distinct thickness dependence [30] of vibrational properties of monolayer systems. To this end, the dependence of the polaronic effect on the layer thickness of the material as well as the effect of interactions involving various types of phonons on the exciton energy need further study. These reasons form the main motivation for this study.

In material systems with *N* atoms per unit cell, three acoustic branches (one longitudinal and two transverse) and three *N*-3 optical branches are present. The monolayer MoS₂, for instance, has the reduced point group symmetry *D*_{3h} associated with 3 atoms per unit cell, and so displays three acoustic and six optical phonon branches. The six optical modes at the *Γ* point in monolayer MoS₂ are classified according to their vibrational and infrared attributes depending on the displacement of the chalcogen atoms

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relative to the metal atoms. Two Raman active modes, A_{1g} and E_{2g}^1 display opposite frequency shifts with layer thickness in MoS_2 [31,32,30]. The A_{1g} mode arises from the out-of-plane displacement of S atoms while the E_{2g}^1 mode is associated with the in-plane but opposing displacements of Mo and S atoms, which experiences dielectric screening of Coulombic interactions [31,32]. Similar trends in the shift patterns of the A_{1g} and E_{2g}^1 frequency modes with change in the number of layers are noted in tungsten dichalcogenides, WS_2 and WSe_2 [33]. Unlike the A_{1g} mode, the E_{2g}^1 is not sensitive to carrier density. This gives rise to differences in the carrier–phonon coupling between the two modes. Phonon energies in the range, $15 \text{ meV} \leq \hbar\omega \leq 70 \text{ meV}$, have been predicted in MoS_2 as well as other transition-metal dichalcogenides in the monolayer form [34,30]. The bulk MoS_2 (2H- MoS_2) on the other hand, possess a point group of higher symmetry D_{6h} due to its center of inversion, with phonon energies in the range, $50 \text{ meV} \leq \hbar\omega \leq 100 \text{ meV}$ [35].

The electron–phonon or hole–phonon coupling due to Fröhlich interaction arises when the polarization of the lattice vibrations are directly coupled to the electron or hole charges [36,37]. This gives rise to the dominant coupling of single carriers with phonons in materials with polar contributions to atomic bonds. However the exciton–phonon interaction is weakened due to the counteracting effects arising from the opposite charges of the electron and hole constituents. For this reason, we focus on the second type of carrier–phonon coupling in which the electron or hole interacts indirectly with the phonons due to deformations in the lattice potential. In this case, the exciton–phonon coupling due to deformation potential is comparable in strength to those of the single carrier–phonon interactions.

In the monolayer MoS_2 , electron scattering and transport dynamics due to electron–acoustic phonon coupling is dominant at low temperatures [15,38]. On the other hand, electron–optical phonon scattering due to deformation potential and Fröhlich interactions dictates the quantum interaction processes at higher temperatures ($>100 \text{ K}$) [39]. In a recent work involving n-type monolayer MoS_2 [40], the hot electron cooling power characteristics revealed a crossover from acoustic phonon dominated cooling at low electron temperatures to optical phonon dominated cooling at higher temperatures (50 to 75 K). To this end, exciton dynamics due to exciton–phonon interaction in the monolayer MoS_2 and other transition metal chalcogenides have yet to be examined in detail. In this work, we examine the characteristics of the excitonic phonon in the monolayer configuration of well known metal chalcogenides based on the acoustic and optical deformation potentials derived from density-functional approaches [34,41,39,32,38]. A microscopic understanding of how the properties of the excitonic polaron are altered in layered metal chalcogenides has potential applications in polariton states arising from linear combinations of exciton and photon states in microcavities and in the decoherence of coherent exciton states in quantum information systems.

The paper is organized as follows. In Section 2, we present the general theory of exciton–phonon interaction in some common monolayer transition metal dichalcogenides. A brief discussion of the challenges in modeling excitonic polarons in materials with a wide range of exciton–phonon coupling is also provided in Section 2. In Section 3, an approximate diagonalization technique involving the total Hamiltonian of exciton, phonon and exciton–phonon interaction energy operators is demonstrated. Analytical expressions of changes in excitonic polaron energy and mass at small exciton wavevectors for deformation potential due to optical phonons are given in Section 4. The analysis of the excitonic polaron properties associated with deformation potential due to acoustic phonons is given in Section 5. Finally, conclusions are

summarized in Section 6.

2. Exciton–phonon interaction in the monolayer transition metal dichalcogenides

The modeling of excitonic polarons in solid state systems using standard techniques is generally challenging due to lack of a simple and unified scheme that remains valid for a wide range of exciton–phonon coupling dynamics. The total Hamiltonian of exciton, phonon and exciton–phonon interaction energy operators appears in a non-diagonal form and requires appropriate diagonalization procedures to derive accurate estimates of the energy eigenvalues and eigenfunctions of the composite exciton–phonon system. In this section, we employ a unitary transformation to diagonalize the exciton–phonon interaction operator. The mass and energy shifts of the transformed ground state excitonic polaron are then evaluated for some common monolayer transition metal dichalcogenides.

We note the critical points in the band gap region where the excitonic interactions with phonons become important for detailed analysis of the polaronic effect. A direct band gap involving the conduction and valence band extrema at the K point occurs in the monolayer configuration of transition-metal dichalcogenides (MX_2). An energy minimum occurs at the Q point along the $K - \Gamma$ axis at the lowest conduction band while a peak for the valence band is located at the Γ point [41]. The acoustic and optical deformation potential estimates for electron–phonon and hole–phonon of monolayer MX_2 at the critical points K , Q , Γ based on density functional theory [41] will be used to estimate the polaronic effect in monolayer excitons.

We consider an isolated exciton moving in a two-dimensional slab representing the monolayer, and interacting with two-dimensional phonons. The total Hamiltonian of the composite system of exciton and LO-phonons can be written as

$$\hat{H} = \hat{H}_{ex}^{2D} + \hat{H}_{ph} + \hat{H}_{ex-ph}^{2D} \quad (1)$$

The term \hat{H}_{ex}^{2D} denotes the quasi-two dimensional exciton Hamiltonian given by

$$\hat{H}_{ex}^{2D} = \sum_{\mathbf{K}} E^{ex}(\mathbf{K}) B_{\mathbf{K}}^{\dagger} B_{\mathbf{K}} + \hat{H}_z, \quad (2)$$

where $B_{\mathbf{K}}^{\dagger}$ ($B_{\mathbf{K}}$) denotes the creation (annihilation) operator of an exciton. The two-dimensional exciton wavevector is denoted by \mathbf{K} which exists in the monolayer plane that constitutes the transition metal (M) and the chalcogen (X) atomic planes. The first term in Eq. (2) is diagonal in the exciton operators as the exciton propagates freely in the monolayer plane. The energy of the exciton in the layered slab given by

$$E^{ex}(\mathbf{K}, \rho_{\parallel}) = E_g + \frac{\hbar^2 \mathbf{K}^2}{2M^*} - E_b(\rho_{\parallel}) \quad (3)$$

E_g is considered to be the band gap along the Σ - K direction in the monolayer MX_2 , and $M^* = m_e^* + m_h^*$ is the effective exciton mass. $E_b(\rho_{\parallel})$ is the exciton binding energy due to Coulomb interaction between the electron and hole within the plane of the monolayer surface.

In Eq. 2, \hat{H}_z denotes the exciton Hamiltonian corresponding to the z direction

$$\hat{H}_z = \frac{p_{e,z}^2}{2m_e} + \frac{p_{h,z}^2}{2m_h} + V_e(z_e) + V_h(z_h) - E_b(z) \quad (4)$$

where $P_{e,z}$ and $P_{h,z}$ are the momentum components associated

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