Excitonic complexes in low dimensional transition metal dichalcogenides

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We examine the excitonic properties of layered configurations of low dimensional transition metal dichalcogenides (LTMDCs) using the fractional dimensional space approach. The binding energies of the exciton, trion and biexciton in LTMDCs of varying layers are analyzed, and linked to the dimensionality parameter \( \alpha \), which provides insight into critical electro-optical properties (relative oscillator strength, absorption spectrum, exciton-exciton interaction) of the material systems. The usefulness of \( \alpha \) is highlighted by its independence of the physical mechanisms underlying the confinement effects of geometrical structures. Our estimates of the binding energies of exciton complexes for the monolayer configuration of transition metal dichalcogenides suggest a non-collinear structure for the trion and a positronium-molecule-like square structure for the biexciton.

I. INTRODUCTION

Transition metal dichalcogenides \( \text{MX}_2 \) (Transition metal \( \text{M} = \text{Mo, W, Nb}; \text{Chalcogen} \ X = \text{S, Se}) \) are currently studied with renewed interest due to their attractive opto-electronic properties and advances in fabrication techniques involving exfoliation into single and multilayer layered configurations known as LTMDCs. These material systems present potential applications in optics, sensing, chemical and biological systems, and quantum informatics and spintronics. In TMDCs, the M metal layer is sandwiched between two X layers with strong intra-plane bondings and weak inter-plane interactions giving rise to the low dimensional, highly anisotropic hexagonal arrangement of M and X atoms with spacegroup \( P6_3/mmc \) associated and the space group number 194. While TMDCs exhibit some properties that complement those of graphene which possess a similar honeycomb pattern of arrangement of atoms, there exist other unique features that do not match. For instance, there is absence of bandgap in graphene while TMDCs are amenable to band-gap engineering properties with potential to act as suitable inorganic substitutes for graphene based applications.

Depending on the number of lattice layers constituting the material, LTMDCs display crossovers in the spectral characteristic of their band-gaps due to the inversion symmetry breaking of the lattice structures. The presence of direct band-gap is evidenced by strong photoluminescence in the vicinity of the \( K \) and \( K' \) points of the Brillouin zone. Similar crossovers are also observed in WSe\(_2\) and WS\(_2\) as the thickness of the material is reduced.

Excitonic features are pronounced in monolayer LTMDCs as a result of their large binding energies which occur due to two main effects: (i) decreased thickness of the material system results in increased interactions between charges and a dimensionality dependent macroscopic surface self-polarization term gives rise to an increased electron-electron correlation and reduced screening effects. The subsequent increase in the quasiparticle gap can be correlated with high exciton binding energies. (ii) The enhanced electron-hole overlap due to the geometrical confinement of exciton wave functions in the reduced dimensional space results in large exciton binding energies. The existence of robust electron-hole correlated states in inorganic LT-MDCs provide viable alternatives to stable exciton states which commonly occur in organic molecular systems. The geometrical confinement of exciton wave functions within a small space region enhances optical densities and oscillator strengths, and supports the existence of exciton complexes such as trions and biexcitons that are stable at room temperatures.

Using two-photon excitation spectroscopy and density functional methods based on the GW-Bethe Salpeter equation (GW-BSE) approach, the exciton binding energy was estimated to be as high as 0.7 eV in Tungsten Disulfide (WS\(_2\)). In Molybdenum Disulfide (MoS\(_2\)), the incorporation of electron-hole interactions within the BSE approach revealed \( A \) and \( B \) excitons linked to two monolayer peaks at respective positions, 1.78 eV and 1.96 eV. These spectral features are consistent with experimental results, and yield exciton binding energies of 0.85 eV in agreement with the binding values computed by Cheiwchanchamnangij et al. First-principles calculations based on the GW-BSE approach, and incorporating excitonic and electron-phonon effects yield exciton binding energies of 0.96 eV. By including both excitonic effects and spin-orbit coupling and larger \( k \)-grid mesh which ensures good convergence during computations, much lower binding energies (< 0.4 eV) were obtained, with \( A \) and \( B \) exciton spectral positions appearing to be in good agreement with experimental results. The incorporation of charge carrier-light coupling element which incorporate optical selection and polarization rules, yield binding energies in the range 0.42-0.44 eV. It thus appear that precise estimates of the exciton binding energies in monolayer LTMDCs remain elusive, with a range of binding energies predicted for the prototype MoS\(_2\) of varying dimensions. A full comparison of the binding energies from various groups which utilized first-principles many-body calculations and experimental techniques are shown in Table-I of Section II.

The discrepancies in the exciton binding energies reported by different groups may arise from technical errors such as low \( k \)-point sampling and neglect of spin-orbit interaction as discussed in Ref. Excitonic binding energies require a dense \( k \)-point mesh to converge and produce reliable results, which can be computationally demanding. The electronic processes which
occurs on the surfaces of the slab-like structures of LTMDCs differ from those in bulk solids, with a potential source of error due to inaccurate estimation of the macroscopic screening in systems with finite width. The shift of surface plasmons due to confinement effects shows the need to account for convergence of the electronic surface with respect to number of monolayers in many-body calculations. Currently available density functionals do not fully incorporate the strong Coulomb interactions and non-local correlations between the 3d and 4s electrons of the transition metal atoms.

In Molybdenum Disulfide (MoS$_2$), the intra-plane bonding within the S-Mo-S structure is known to give rise to mixing of s, p and d orbitals of Mo with the p orbital of S. These mixing effects change when the number of lattice layers making up the material system is altered. There are corresponding changes to the surface charge distribution, which are normally not fully incorporated in density functional computations. Therefore, there exist several sources of errors that need to be addressed before exciton binding energies can evaluated with greater accuracy in LTMDCs. Current experimental techniques are unable to perform a direct measurement of exciton binding energies, which underpins the importance of ab initio computational methods that provide an indirect mode of evaluating the binding energy.

In this study, we adopt an approach based on fractional dimension to examine exciton binding energies in LTMDCs. The fractional dimensional space approach (FDSA) has been utilized in studies of excitonic properties by fitting to models that utilizes a variable dimension, $1 \leq \alpha \leq 4$ which provide good agreement with experiments findings. The pseudo-two-dimensionality attribute of the exciton simplifies the evaluation of electro-optical properties. This is performed by the mapping of the anisotropic exciton in the real space into an isotropic environment parameterized by a single quantity, $\alpha$. The usefulness of $\alpha$ can be appreciated by the fact that it is independent of the physical mechanisms governed by confinement effects arising from specific geometrical structures. Consequently a particular optical spectrum can be attributed to different systems as long as these possess the same dimensionality. In earlier works, the exciton binding energy and characteristics of the optical spectrum, exciton-exciton interaction strength, properties of donor states, and exciton-phonon coupling have been determined using the dimensionality parameter, $\alpha$.

The parameter $\alpha$ takes into account the tunneling effects so that the exact two-dimensional exciton model is best valid at a critical confinement length, depending on the material composition and other external conditions related to electric and magnetic fields. The use of a rigid exciton model for which $\alpha = 2$ or 3 can give rise to an overestimation of the exciton binding energies. Excitons described by fractional values of $\alpha$ are able to provide realistic values of the binding energy, however it is important that $\alpha$ is defined using appropriate material parameters. In this study, we show that the FDSA provides an intuitive approach to understanding the optical features that are affected by a change in the number of layers comprising LTMDCs. We highlight the convenient estimation of the binding energies of charged exciton complexes and biexcitons using analytical relations based on the FDSA.

II. EXCITONS IN FRACTIONAL DIMENSIONAL SPACE

In a fractional dimensional space described by the parameter $\alpha$, the relative motion of a correlated electron-hole pair with generalized coordinates $r, \theta$ appear as

$$[-\frac{\hbar^2}{2\mu} \frac{1}{r^{\alpha-1}} \frac{d}{dr} \left( r^{\alpha-1} \frac{d}{dr} \right) - \frac{e^2}{4\pi\varepsilon r} - \frac{\hbar^2}{2\mu r^2 \sin^{\alpha-2}\theta} \frac{d}{d\theta} \left( \sin^{\alpha-2}\theta \frac{d}{d\theta} \right)] \times \Phi(r, \theta) = E \Phi(r, \theta),$$

(1)

where the exciton reduced mass $\mu^{-1} = m_e^{-1} + m_h^{-1}$, and $m_e$ and $m_h$ being the effective masses of the electron and hole, respectively. The exciton wavefunction can be separated as $\Phi_n(r, \theta) = \psi_n(r)\Psi(\theta)$ where $\Psi(\theta)$ denotes an eigenfunction of the angular momentum $L^2$, $L^2\Psi(\theta) = l(l + 2)\Psi(\theta)$. The quantum number, $n = 1, 2, \cdots$, is the principal quantum state. The decoupling of $\Phi_n(r, \theta)$ allows Eq. 1 to be split into two independent equations, with only one that depends on the energy of the exciton. The 1s state of an exciton in an $\alpha$D space appear as

$$\psi_{1s}(r) = \left[ \frac{2^\alpha \pi}{\Gamma(\frac{\alpha+1}{2})} \frac{1}{a_B^\alpha} \right]^{\frac{1}{2}} \exp \left[ -\frac{2}{\alpha-1} \frac{r}{a_B} \right]$$

(3)

with the binding energy

$$E_{\text{BX}} = \frac{R_g}{(n + \frac{a_B^2}{\alpha})^2},$$

(4)

where $a_B = 0.529 \times 10^{-10}$ m is the three-dimensional Bohr radius of the exciton, and $R_g = 13.6 \frac{2}{\alpha}$ eV is the effective exciton Rydberg energy. The exciton reduced mass $\mu$ is given in terms of the free-electron mass. The parameter $\alpha$ is dependent on the variables.
used to describe the dimensionality of the confined exciton. The mapping of layered low dimensional LTMDCs into the effective fractional-dimensional space may be performed by utilizing the dimensionality based on the ansatz, \( \alpha = \gamma_x + \gamma_y + \gamma_z \) where \( \gamma_i \) (i= x, y, z) denotes the measure of confinement in the x, y, and z, respectively. As there is no restriction to motion in the x, y plane of layered structures, we get \( \gamma_x = \gamma_y = 1 \). In the direction where there is confinement, we employ the relation, \( \gamma_z = 1 - \exp[-\chi] \) where

\[
\chi = \frac{\text{confinement length}}{\text{effective interaction length}}
\]

This gives rise to an enhanced Coulomb interactions between the charge carriers resulting in increased exciton binding energies. Using Eq. 5, we obtain the well known expression for \( \alpha \) applicable to two-dimensional heterostructures such as the infinite quantum wells of confinement width \( L_w \).

\[
\alpha = 3 - \exp\left(-\frac{L_w}{2a_B}\right).
\]

Eq. 6 needs to be modified in the case of finite quantum wells where there is penetration of the carriers wavefunction into regions outside the well. In LTMDCs where there is crossover from an indirect band-gap to a direct band-gap with decreased thickness, carrier dependent parameters such as the effective mass, dielectric constants, and location of \( K \) points need to be incorporated for accurate evaluation of \( \alpha \). In this study, we propose the dimensionality, \( \alpha \), based on the ratio of the effective exciton Rydbergs, \( \beta \)

\[
\alpha \approx 2\sqrt{\beta} + 1
\]

\[
\beta = \frac{R^{3D}_y}{R^{3D}_x}
\]

In bulk material systems, \( R^{3D}_y \rightarrow R^{3D}_x \), we obtain \( \alpha = 3 \) and \( E^{E_X}_n = E^{3D}_X \) for the ground state \((n = 1)\). In lower dimensional systems such as monolayer and bilayer LTMDCs, the dielectric constant is decreased resulting in larger effective Rydbergs, \( R^{nD}_y > R^{3D}_y \), with \( \alpha < 3 \). Eq. 7 incorporates the dependency of \( \alpha \) on the dielectric environment and effective exciton mass altered by confinement effects.

In Table-I, we compare the exciton binding energies at the \( K \) high symmetry points of the Brillouin zone of monolayer MoS\(_2\) reported in earlier studies, and our estimates obtained by using available \( \mu, \epsilon \) and \( E^{E_X}_0 = 13.6 \ \mu/eV \). We provide brief descriptions related to the convergence parameters, as well justification for our use of the dielectric parameters in Table-I. The exciton radius \( \approx 9 \ \text{Å} \) appears to be a consistent estimate in earlier works as well as from our choice of \( \mu, \epsilon \) for the monolayer MoS\(_2\) system. The change in dimensionality \( \alpha \) of materials of varying layer numbers is analyzed using Eqs.7 and 8. The dimensionality, \( \alpha = 3 \) is computed using Eq.7 with the bulk Rydberg \( R^{3D}_y \) estimated using \( \mu = 0.433 \) and \( \epsilon = 10.744 \). We expect slight variations in \( \alpha \) to occur for \( \mu, \epsilon \) that depart from our estimates used to compute \( R^{3D}_y \). Nevertheless, the qualitative features highlighted by the increase in \( \alpha \) with increase in the number of layers is expected to remain intact. The main result of this study is thus the demonstration of the gradual increase in \( \alpha \) from 2 in monolayers, to intermediate values (2.30 < \( \alpha < 2.69 \)) in bilayer and 4-layer MoS\(_2\) system to the standard reference, \( \alpha = 3 \) in bulk MoS\(_2\). It is to be noted that we have employed \( \mu \) in the range (0.2 - 0.3) to compute \( \alpha \) for the bilayer, 4-layer and 6-layer MoS\(_2\) system, due to unavailability of \( \mu \) values for these systems.

Table-I highlights the discrepancies between the binding energy estimates in some earlier works and our estimates based on \( E^{E_X}_0 \) for the monolayer MoS\(_2\) system. By using \( \alpha = 3 \) in bulk MoS\(_2\), the energy range of 0.2 - 0.3 eV (\( \alpha \approx 2 \)) provides reasonable estimates of the binding energy of MoS\(_2\) in the monolayer configuration at \( \alpha = 2 \). Hence one underlying reason for disparities in binding energies for the monolayer configuration as shown in Table-I can be attributed to an underestimation of the dimensionality parameter \( \alpha \) in the MoS\(_2\) system. This gives rise to an overestimation of the exciton binding energy as noted in some works. Other contributing factors may arise due to variations in experimental conditions, convergence criteria, dielectric tensor estimates, choice of the crystal lattice constants (a and c) and the separations between the monolayers.

### A. Change of dielectric properties with \( \alpha \)

Table-I shows the difference in dielectric constants between the monolayer, bilayer and the bulk MoS\(_2\) system. There is decrease in dielectric components, \( \epsilon_L, \epsilon_L \) with the dimensionality \( \alpha \), which is consistent in all cited works. In low-dimensional LTMDCs, the decrease of \( \epsilon \) with \( \alpha \) can be examined by considering each monolayer of M (= Mo, W, Nb) and Chalcogen X (= S, Se) atoms as a homogeneous dielectric slab of thickness \( t \) with a bulk dielectric constant \( \epsilon_m \). We note that in practical situations,
TABLE I: Comparison of exciton binding energies at the $K$ high symmetry points of the Brillouin zone of monolayer MoS$_2$ based on earlier studies and our theoretical prediction using $E_{bhX}$ = 13.6 µ/$\epsilon^2$ eV. The change in the dimensionality $\alpha$ of materials of varying layer numbers is analyzed using Eqs. [7] and [8]. The exciton effective mass is denoted by $\mu$ and the ratio $\sigma = \frac{m_c}{m_h}$. The exciton effective mass and dielectric constants employed to determine the energy estimates are included. In Ref. the density-functional theoretical calculations included spin-orbit coupling effects, using a large k-grid mesh ($> 18 \times 18$). The GW-Bethe Salpeter equation (GW-BSE) approach in Ref. incorporates self-energy, excitonic, and electron-phonon effects but utilizes comparatively smaller k-grid mesh ($12 \times 12$). Refs. adopt small k-grid mesh ($\leq 12 \times 12$) while the computation in Ref. involve a k-grid mesh of $15 \times 15$. The electron and hole masses provided for Ref. are the average of the $K_1$ (longitudinal) and $K_1$ (transverse) symmetry points of the Brillouin zone. The pair of exciton mass values for Ref. correspond respectively to the renormalized spin-down and spin-up valence effective band masses due to spin-orbit coupling, and the pair of binding energies correspond respectively to those of the A and B excitons.

The effective dielectric constant, $\epsilon = \sqrt{\epsilon_{\parallel} \epsilon_{\perp}}$ where $\epsilon_{\parallel}$ ($\epsilon_{\perp}$) denote dielectric components perpendicular (parallel) to the lattice vector in the $z$ direction. $E_{bhX}$ is the exciton binding energy that appear in the cited references, which is compared with our estimate of the binding energy $E_{bhX}$ = 13.6 µ/$\epsilon^2$ eV using $\mu$ and $\epsilon$ provided in the references. Additional notes are provided below when $\mu$ and $\epsilon$ cannot be retrieved from the references. Physical quantities appearing with superscript * are our estimates of $\mu$, $\epsilon$ used to complete evaluation of $E_{bhX}$. The dimensionality, $\alpha$ is computed using Eqs. [7] and [8] with the bulk Rydberg $R_{bX}^D$ ($\alpha = 3$) based on $\mu = 0.45\alpha$ and $\epsilon = 10.7\alpha$. The trion binding energies are estimated using Eq. [12]. All binding energies appear in units of eV.

The experimental value of 0.08 eV in bulk MoS$_2$ is provided in Ref.

†† We use $\epsilon = 3.4^{45}$ (not specified in Qiu et al. $^{33}$) and $\mu = 0.2$ to compute $E_{bhX}$ (Eq. [4]) and $E_{bhX}$ (Eq. [12]). The exciton radius = 9 Å obtained using these values of $\mu$, $\epsilon$ is consistent with the root mean square exciton radius of 10 Å by Qiu et al.$^{33}$

We determine $\epsilon = 3.68$ (not specified in Zhang et al.$^{44}$) based on the measured exciton radius = 9.3 Å at electron density $\approx 2.4 \times 10^{12}$/cm$^2$ in Ref.$^{45}$

We determine $\alpha$ and $E_{bhX}$ based on $\mu = 0.27^a$ and $\epsilon = 3.68^b$.

$^{d2}$ We compute $\epsilon$ and $E_{bhX}$ based on $\mu = 0.28^d$ and the transverse component of the macroscopic static dielectric tensor, $\epsilon = 3.68^{d2}$.

$^c$ $\mu$, $\sigma$ are computed using band edge masses, $m_h = 0.5$, $m_h = 0.6$ retrieved from Zhang et al.$^{45}$

We compute $\epsilon$ and $E_{bhX}$ based on $\mu = 0.28^{d1}$ and the transverse component of the macroscopic static dielectric tensor, $\epsilon = 3.68^{d2}$.

$^d$ $\mu$, $\sigma$ are computed using electron and hole effective masses at $K$ points for optimized lattices, $m_c = 0.32$, $m_h = 0.37$ obtained from Shi et al.$^{44}$

| No. of Layers | $\mu$ | $\sigma$ | $\epsilon_{\parallel}$, $\epsilon_{\perp}$, $\epsilon$ | $E_{bhX}$ | $\alpha$ (Eq. [7], [8]) | $E_{bhX}$ (13.6 µ/$\epsilon^2$ eV) | $E_{bhX}$ (Eq. [12]) |
|---------------|-------|---------|---------------------------------|----------|---------------------|------------------|-----------------|
| monolayer     | 0.13  | 0.80    | $3.43^{11}$                     | 0.96$^f$ | 1.95                | 0.21             | 0.021           |
| bilayer       | 0.19  | 0.80    | 4.2, 2.8, 3.43                  | 0.897    | 1.92                | 0.22             | 0.022           |
| bulk          | 0.4$^{44}$ | 0.80 | 13.5, 8.5, 10.71                | 0.025    | 3.0                 | 0.04 (0.08$^c$)  | < 0.005         |
| monolayer     | 0.25  | 0.54    | $3.76^f$                        | 1.89     | 0.24                | 0.024            |                 |
| monolayer     | 0.2$^*$| 0.83$^a$| $3.68^b$                        | 0.28 - 0.33 | 1.83$^c$             | 0.27$^c$         | 0.032$^{45}$   |
| monolayer     | 0.28$^{0.26}_{0.03}$ | 0.83$^a$ | $3.68^b$                        | 0.42, 0.44 | –                  | –                |                 |
| monolayer     | 0.28$^{0.26}_{0.03}$ | 1.11  | $4.26^{d2}$                     | 0.85     | 1.95$^{d1}$         | 0.21$^{d1}$      | 0.021           |
| monolayer     | 0.17$^e$ | 0.86$^b$ | –                               | 0.54     | –                  | –                |                 |
| monolayer     | 0.20 - 0.25$^*$ | ~ 0.8$^*$ | $6.9, 4.4, 5.51$               | –        | 2.45 - 2.30         | 0.09 - 0.11      | < 0.01          |
| monolayer     | 0.25 - 0.3$^*$ | ~ 0.8$^*$ | $8.7, 5.9, 7.16$               | –        | 2.69 - 2.42         | 0.07 - 0.09      | < 0.01          |
| monolayer     | 0.25 - 0.3$^*$ | ~ 0.8$^*$ | $9.8, 6.4, 7.92$               | –        | 2.87 - 2.58         | 0.05 - 0.08      | < 0.01          |
| monolayer     | 0.020$^{27}$ | 0.030$^{69}$ | –                               | –        | –                  | –                |                 |

The monolayer LTMDC material is sandwiched between two regions of different dielectric constants. For the simple model configuration of repetitive multi-layers with a vacuum interlayer separation, $D$, the composite dielectric components for the configuration of repetitive layers appear as $\epsilon_{\parallel} = \eta (\epsilon_{m} - 1) + 1$, $\epsilon_{\perp} = 1 - \frac{4\alpha(\epsilon_{m} - 1)}{\epsilon_{m}}$ where $\epsilon_{\parallel}$, $\epsilon_{\perp}$ denote dielectric components parallel (perpendicular) to the layers. The parameter $\eta = \frac{D}{\epsilon_{\parallel}}$ provides the anisotropic measure of the layered system, so that $\eta = 1$ represents the bulk system and a critical $\eta = \eta_c$ corresponds to the monolayer configuration. By setting $\epsilon_{m} = 10.7^{44}$ and evaluating the relations $\epsilon_{\parallel}$, $\epsilon_{\perp}$ as function of $\eta$, the interpolation between the bulk MoS$_2$ and the monolayer LTMDC can be analyzed to reveal the decrease of $\epsilon$ with $\eta$ (or $\alpha$).
The excitonic photoluminescence spectra can be analyzed via the absorption coefficient derived in fractional dimensional space\textsuperscript{33}

\[
O(h\omega) = O_0 \left[ \sum_{n=1}^{\infty} \frac{F_1(n, \alpha) R_y}{(n + \frac{\alpha - 3}{2})^{\alpha + 1}} \delta(h\omega - E_n) + |\Gamma(\frac{\alpha - 1}{2} + i\gamma)|^2 \frac{e^{\pi \gamma}}{\pi} \gamma^{2-\alpha} \Theta(h\omega) \right]
\]

(9)

\[
O_0 = \frac{F_2(\alpha)}{n_\mu c m^2 \omega n c v R_y} \left[ \frac{2 |d_{cv}|^2 L_c^\alpha}{\alpha - 2} \right]
\]

(10)

where \(h\omega\) is the photon energy, and \(F_1(n, \alpha)\) and \(F_2(\alpha)\) are explicit functions of \(\alpha\). \(\Theta(h\omega)\) is the Heavyside step function, the reduced parameter \(\gamma = \sqrt{R_y/h\omega}\) and \(n_\mu\) is the refractive index of the material. \(L_c\) is the effective length of the material, \(|d_{cv}|^2\) is the conduction-to-valence squared matrix element of the electron dipole moment, \(c\) is the velocity of light, and \(\Gamma(x)\) is the Euler gamma function. The absorption coefficient in Eq. (9) reduces to the expected expression in the exact 2D and 3D cases.

The parameter \(\alpha\) establishes a strong correlation between the exciton binding energy and the absorption coefficient in Eq. (2). According to the \(\alpha\) values evaluated for the number of layers making up the MoS\(_2\) system in Table-I, it can be seen that there is decrease in \(\alpha\) from the bulk, to the 4-layer and bilayer and finally the monolayer configuration. Following Eq. (11), we expect to obtain an enhancement in the optical densities and oscillator strengths as the number of layers is decreased until the monolayer configuration is reached. Likewise, changes in exciton-phonon interactions\textsuperscript{33}, stark-shifts due to the application of an external electric field\textsuperscript{32} and exciton-exciton interaction strength\textsuperscript{32} are expected when the number of layers in LTMDCs are reduced.

### III. TRIONS AND BIEXCITONS IN LTMDCS

#### A. Charged excitons

Charged exciton complexes such as negative \(X^-\) and positive \(X^+\) trions are formed when a single exciton is correlated respectively, with an additional electron or hole. Two-dimensional trions have a binding energy which is about an order-of-magnitude larger than that of the bulk trions due to confinement effects. In a recent experiment involving monolayer MoS\(_2\)\textsuperscript{27} there was formation of stable trion states with a binding energy of 20 meV when the population of excess electrons was increased. A higher binding energy of 30 meV was noted in a recent work\textsuperscript{55}, stark-shifts due to the application of an external electric field\textsuperscript{32} and exciton-exciton interaction strength\textsuperscript{32} are expected when the number of layers in LTMDCs are reduced.

In our earlier work, the collinear structure of the trion was used to derive as simple relation relating the ratio of the trion to exciton binding energies as\textsuperscript{22}

\[
\frac{E_{b,X^-}}{E_{b,X}} = \frac{9}{4} \left( \frac{2\sigma + 1}{\sigma^2 + 4\sigma + 2} + 1 \right)^{-1} - 1
\]

(11)

Eq. (11) is applicable to the trion configuration with the hole (electron) at the midpoint of two electrons (holes) in negatively (positively) charged trion. In the case of the monolayer MoS\(_2\), \(\sigma \approx 0.8 - 1\), and we obtain typical trion binding energies, \(E_{b,X^-} \approx 0.5 \ E_{b,X}\), which compares well with \(E_{b,X^-} \approx 0.4 \ E_{b,X}\) obtained using the variational quantum Monte Carlo approach\textsuperscript{22}. These relations would however yield much higher binding energies \(\sim 100\) meV (than currently observed 20 to 30 meV\textsuperscript{27,69}) for typical exciton binding energy of \(> 0.2\) eV in the monolayer MoS\(_2\) system. Therefore the collinear structure of the trion does not adequately describe the charged exciton complex in LTMDCs.

Due to the Pauli exclusion principle, the multiple occupation of single fermion states is forbidden. The trion trial wavefunction should therefore incorporate parameters linked to the phase space surrounding the exciton\textsuperscript{27,73} for accurate energy convergence in variational calculations\textsuperscript{21}. To this end, the excess electron added to form a trion is more likely to move in the direction perpendicular to the monolayer surface, and bind to the two-dimensional exciton located within the monolayer. A hyper-spherical approach considered by Ruan et. al.\textsuperscript{74} incorporates the possibility of modification of charge interactions in the \(xy\) plane due to existence of charges outside the monolayer. Ref.\textsuperscript{74} predicts the following relation between the trion and exciton binding energies

\[
E_{b,X^-} \approx 0.1E_{b,X} \quad \sigma > 0.6
\]

(12)

Eq. (12) yields trion binding energies of 20-30 meV which are consistent with experimental observations\textsuperscript{27,69}. In Table-I, we have compared the negative charged exciton binding energies (Eq. (12)) with experimentally observed values, and also provided
estimates of the binding energy for other configurations of the MoS$_2$ system. The negatively charged trion may be difficult to resolve in the high dimensional ($\alpha > 2.5$) bulk and systems which exceed 4-layer thickness, however there is good possibility of its detection in 2-layer materials. The predicted trion binding energies for other systems are presented in Table-II. Similar to the MoS$_2$ monolayer system, the mass ratio $\sigma$ is close to unity for other LTMDCs. This fact will be employed in the evaluation of the binding energies of the biexciton in the next section.

### B. Biexcitons

The energy of the biexciton, a four-body system of two electrons and two holes, is dependent on the degree of its confinement and the electron-to-hole ratio $\sigma = \frac{m_e}{m_h}$ of effective masses. Confinement effects play an important role in strengthening the biexciton binding energy. The ratio of biexcitonic $E_{biX}$ to excitonic $E_{ex}$ binding energies, $\gamma_b = \frac{E_{biX}}{E_{ex}}$ was shown as a monotonic function of the dimensionality $\alpha$. By optimizing the geometric configuration of a simple model structure of the biexciton where confinement effects are neglected, Oh et. al. obtained $\gamma_b \approx 0.23$ at $\alpha \approx 1$. The configuration of the biexciton assumes a positronium-molecule-like square structure with $\frac{m_e}{m_h} = 0.82$, $\frac{m_e}{m_h} = 0.58$.

Numerical results show that dependence of $\gamma_b$ on the mass fraction $\sigma$ may be ignored for $\sigma$ values in the range of $\approx 0.8 - 1$. A relation linking the biexciton energies to $\alpha$ has been obtained for $\sigma = 0.1$ as:

$$E_{biex}(\alpha) = \sum_{i=1}^{5} \frac{c_i}{\alpha^{i-1}} \exp(-\alpha)$$

where the coefficients $c_i$ which varies according to $\alpha$ are provided in Ref. 61. We use a definition for the biexciton binding energy based on the energy released when a biexciton is formed from two excitons

$$E_{biX}(\alpha) = 2E_{ex}(\alpha') - E_{biex}(\alpha')$$

where $E_{ex}(\alpha')$ is the dimensionality dependent single exciton energy. A negative $E_{biX}$ indicates that the biexciton is stable and is not likely to dissociate into two separate excitons. It is important to note that a pair of excitons in two-dimensional space may be not necessarily bind to form a biexciton with strictly two-dimensional attributes (i.e. $\alpha \neq \alpha'$). We use Eqs. 13 and 14 to estimate the biexciton binding energy

$$E_{biX} = 0.2E_{ex} \quad \sigma \approx 1$$

which yields a ratio that is consistent with $\gamma_b \approx 0.23$ obtained by Oh et. al. 51. The pseudo two-dimensional biexciton has a much larger binding energy compared to the bulk biexciton. An earlier work showed that the biexciton binding energy increases more rapidly than the excitonic binding energy when confinement is enhanced. In the case of the monolayer MoS$_2$, Mai et. al. obtained an experimental estimate of 70 meV, and numerical binding energies in the range of 35 - 140 meV. These values agree reasonably well with our estimated range of 40 - 80 meV (Eq. 15) for the biexciton binding energy, by considering the exciton binding energy to be in the range, 0.2 - 0.4 eV (see Table-I). The biexciton binding energies for other Mo and W-family dichalcogenides are presented in Table-II. It can be seen that the selenides have higher static dielectric values compared to the sulfides, but with comparable exciton effective masses. Consequently the exciton, trion and biexciton binding energies of monolayer MoS$_2$ are higher than those of MoSe$_2$. The larger exciton effective mass of MoS$_2$ also results in higher binding binding energies than those of WS$_2$.

The binding energies of the biexciton and trion systems in Table-I and Table-II show the close spectral proximity of the exciton complexes to the exciton quasiparticle for various configurations of the LTMDCs. In particular, the binding energies of the trion and biexciton complex quasiparticle for the monolayer configuration suggest favorable conditions for the existence of the exciton-trion-biexciton states as an entangled tripartite state. The specific features of this tripartite state is beyond the scope of this study, and will be examined in future investigations.

### IV. CONCLUSION

In summary, we have examined the binding energies of the exciton in two-dimensional and quasi-two dimensional structures using the fractional dimensional space approach. The dimension of the exciton in LTMDCs with different number of layers is considered in fractional space, with the dimensionality parameter $\alpha$ seen to vary between the ideal 2D and 3D limits. The binding energy of exciton is linked to $\alpha$, which underlies the confinement effects of various geometrical structures. The exciton binding energy decreases with increasing number of layers in MoS$_2$, a trend that is noted in other Mo and W family of dichalcogenides. By setting $\alpha = 3$ in bulk MoS$_2$, we obtain exciton binding energies (0.2 - 0.3 eV) ($\alpha \approx 2$) in the monolayer configuration which
is lower than estimates of this quantity reported in earlier works. This energy range is consistent with experimental binding energies of exciton complexes (negatively charged trion, biexciton), as well as estimates based on known analytical relations.

We attribute a likely reason for the disparities in binding energies for the monolayer configuration reported in previous studies to the underestimation of the dimensionality parameter $\alpha$ in MoS$_2$. The main result of this study is the demonstration of the gradual increase in $\alpha$ from 2 in monolayers, to intermediate values ($2.3 < \alpha < 2.6$) in bilayer and 4-layer MoS$_2$ system to the expected value of $\alpha = 3$ in bulk MoS$_2$.

The application of the FDSA to LTMDs is expected to provide insight to critical opto-electronic properties which are altered via adjustment of the number of lattice layers. The simplification provided by the fractional dimensional space approach (FDSA) has expected tradeoffs in terms of not being able to compete with the accuracy of complicated and sophisticated numerical approaches afforded by ab initio density functional techniques. However the scaling feature of the FDSA which appear as a consequence of solving the Schrödinger equation in noninteger dimensions, can be used to track non integer-dimensional occurrences of excitonic attributes as reliable features in computational modeling.

The band gap in MoS$_2$ and other transition metal dichalcogenides can be engineered by altering the number of layers and the dielectric constant of the medium surrounding the layers. The strength of electron-hole coulomb interaction and the exciton binding energy can also be enhanced by using specific geometrical structures such as nanotubes fabricated using transition metal dichalcogenides. The increased dimensionalities of the exciton in such confined systems provide opportunities for selecting attractive electro-optical properties and specific visible features in the optical spectra. Computational studies employing fractional dimensions can therefore be used to analyze optical features in experimental spectra studies, and facilitate the control of optical properties of devices.

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1. Experimental binding energy in Ross et al.\textsuperscript{2,39}\n2. Experimental binding energy in Komsa et al.\textsuperscript{2,40}\n3. Experimental binding energy in Jones et al.\textsuperscript{2,41}\n
TABLE II: Binding energies of the exciton, negatively charged exciton (trion) and biexciton in select monolayer LTMDCs. Estimates for the exciton and biexciton binding energies are obtained using Eq. [13] and [15] respectively. The electron ($m_e$) and hole ($m_h$) masses are retrieved from Shi et al.\textsuperscript{2,42} and the corresponding exciton reduced mass, $\mu$, is compared those calculated using DFT+RPA by Berkelbach et al.\textsuperscript{2,42} (appearing within brackets). $\epsilon$ is computed using $\epsilon_\perp$, $\epsilon_\parallel$ obtained from Kumar et al.\textsuperscript{2,43}.

| System | $m_e$, $m_h$ | $\mu$ | $\sigma$ | $\epsilon_\perp$, $\epsilon_\parallel$, $\epsilon$ | $E_{bX}$ (13.6 $\mu$/$\epsilon^2$) | $E_{bx}$ – (Eq. [12]) | $E_{bx}$ (Eq. [15]) |
|--------|--------------|--------|----------|---------------------------------|-------------------------------|--------------------------|--------------------------|
| WS$_2$ | 0.24, 0.31   | 0.14 (0.16) | 0.77     | 4.4, 2.9, 3.57                   | 0.14                          | 0.014                    | 0.03                     |
| MoSe$_2$ | 0.36, 0.42   | 0.19 (0.27) | 0.86     | 6.9, 3.8, 5.12                   | 0.10, 0.78\textsuperscript{a} | 0.01, 0.03$^3$         | 0.02                     |
| WSe$_2$ | 0.26, 0.33   | 0.15 (0.17) | 0.79     | 4.5, 2.9, 3.61                   | 0.15                          | 0.015, 0.03$^3$         | 0.03                     |

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\begin{itemize}
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