Two-dimensional excitons in monolayer transition metal dichalcogenides from radial equation and variational calculations

J-Z Zhang and J-Z Ma

School of Physics, Jilin University, Changchun 130012, People’s Republic of China

E-mail: phyjzzhang@jlu.edu.cn

Received 14 November 2018, revised 9 December 2018
Accepted for publication 17 December 2018
Published 21 January 2019

Abstract

Exciton energy spectra of monolayer transition metal dichalcogenides (TMDs) in various dielectric environments are studied with an effective mass model using the Keldysh potential for the screened electron–hole interaction. Two-dimensional (2D) excitons are calculated by solving a radial equation (RE) with a shooting method, using boundary conditions that are derived by applying the asymptotic properties of the Keldysh potential. For any given main quantum number \( n \), the exciton Bohr orbit shrinks as \( |m| \) becomes larger (\( m \) is the orbital quantum number) resulting in increased strength of the electron–hole interaction and a decrease of the exciton energy. Further, both the exciton energy and its effective radius decrease linearly with \( |m| \). The screened hydrogen model (SHM) (Olsen et al 2016 Phys. Rev. Lett. 116 056401) is examined by comparing its exciton energy spectra with our RE solutions. While the SHM is found to describe the nonhydrogenic exciton Rydberg series (i.e. the energy’s dependence on \( n \)) reasonably well, it fails to account for the linear dependence of the exciton energy on the orbital quantum number. The exciton effective radius expression of the SHM can characterize the exciton radius’s dependence on \( n \), but it cannot properly describe the exciton radius’s dependence on \( m \), which is the cause of the SHM’s poor description of the exciton energy’s \( m \)-dependence. Analytical variational wave-functions are constructed with the 2D hydrogenic wave-functions for a number of strongly bound exciton states, and very close exciton energies and wave-functions are obtained with the variational method and the RE solution (exciton energies are within a 6% of deviation). The variational wave-functions are further applied to study the Stark effects in 2D TMDs, with an analytical expression derived for evaluating the redshift the ground state energy.

Keywords: excitons, monolayer transition metal dichalcogenides, effective mass model, variational method, Stark effect

(Some figures may appear in colour only in the online journal)
on wavevector $\mathbf{q}$ for small $g$ [15], $\varepsilon(q) = 1 + 2\pi\alpha_{2D}q$ ([16]), where $\alpha_{2D}$ is the 2D polarizability of the monolayer, leading to dielectric screening that is nonlocal in real space. The nonlocal screening has a twofold influence on the excitonic energy levels. First, the reduced screening in two dimensions enhances the $e-h$ interaction making excitons in TMDs have a large binding energy, ranging from several tenths of an eV to 1 eV. Second, the screened $e-h$ interaction due to the dielectric function $\varepsilon(q)$, namely the Keldysh interaction [16, 17], differs from the usual 2D Coulomb interaction, and thus 2D exciton energy levels are expected to deviate from the Rydberg series of a 2D hydrogen model (2DHM). This prediction has been experimentally confirmed by several experimental studies, with optical spectroscopy measurements performed on ML WS$_2$ on a SiO$_2$ substrate [6, 13] and also for ML WSe$_2$ on a SiO$_2$ substrate [14].

A rigorous treatment of 2D excitons is the use of the Bethe–Salpeter equation (BSE) based on a first-principles GW quasiparticle band structure [3, 5, 18–21]. For ML TMDs in a dielectric environment, for instance, on a substrate, however exciton calculations become intractable with a standard GW plus BSE approach and have resort to simplified models such as the effective mass model. While most calculations are focussed on the exciton ground states of ML TMDs only a few theoretical studies have been carried out for strongly bound excitons [6, 22] and $s$ exciton Rydberg series (i.e. orbital quantum number $m = 0$) [13, 23], and overall there is a lack of calculations of exciton energy spectrum [3, 5]. To calculate exciton energy spectrum analytically, recently Olsen et al have improved the 2DHM to include the nonlocal screening from the 2D crystal and obtained a simple expression for the Rydberg series [3]. In the screened hydrogen model (SHM) of Olsen et al [3], an effective dielectric constant dependent on the excitonic level is defined by averaging the dielectric function $\varepsilon(q)$ mentioned above, linear in $q$, over the extent of the exciton. The SHM has reproduced the nonhydrogenic Rydberg series for the $s$ excitons in a freestanding ML of WS$_2$ [3], but it is unclear as yet whether it can make an accurate description for the entire exciton energy spectrum consisting of a number of $m$ values. Apart from the analytical model such as the SHM, the variational method (VM) is also a simple approach to obtaining exciton states, and it has been used to calculate the 2D exciton ground states for ML TMDs [24]; so far as we know there has been no report on excited state calculation with the VM for ML TMDs.

In this paper, we study 2D exciton energy spectra of a TMD monolayer in various dielectric environments. We calculate exciton states numerically using the effective mass model for the excitonic Hamiltonian. The original SHM deals with a freestanding monolayer so we need to extend it to include screening from the dielectric environment. The SHM is very convenient for 2D exciton evaluation, and one of course wants to know the discrepancy between exciton energy spectra calculated with this model and a more accurate approach. We employ the Keldysh potential to describe the screened $e-h$ interaction, as it is directly related to the specific dielectric function $\varepsilon(q)$ that is averaged in the SHM to give an effective dielectric constant (refer to expressions (9) and (10) in section 2 below), and also this facilitates a proper examination of the SHM against our numerical results. We found that the SHM can describe the nonhydrogenic exciton Rydberg series reasonably well but it cannot properly describe the variation of the exciton energy with the orbital quantum number $m$. In addition, based on our RE solutions, we construct analytical variational wave-functions and obtain analytical expressions for the energy expectation values to easily calculate strongly bound exciton states. Further we show an example of application of these variational wave-functions, and specifically we use them to calculate the Stark effects in ML TMDs.

This paper is organized as follows. In section 2, a formulation of 2D excitons in the effective mass model is presented where the 2D excitonic equation is simplified to a one-dimensional (1D) differential equation, and the boundary conditions are derived by employing the asymptotic properties of the Keldysh potential. Then a shooting method including Runge–Kutta integration is developed for the numerical solution of the 1D radial equation (RE). An extension of the SHM to account for screening from the dielectric environment is also described. In section 3, first we present the results of the exciton energy spectrum of a freestanding ML of MoS$_2$ from the numerical solution of the 1D RE, and then compare with the exciton energy spectrum from the SHM. We then compare several strongly bound exciton states of ML MoS$_2$ on various substrates calculated with these two approaches (i.e. 1D RE and SHM) and our VM. Then, we show results of the 2D excitons in ML WS$_2$ on the SiO$_2$ substrate calculated with the three approaches and comparisons with the experimental data. Further we present Stark effects in ML TMDs such as the energy shifts and level splitting obtained with our variational wave-functions. Finally, section 4 summarizes the main results obtained.

2. Model

2.1. Excitonic radial equation

Within the effective mass model, the excitonic Hamiltonian can be written as [24–28]

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 - V(r),$$

where $\mathbf{r} = (x, y)$ is the position vector in the plane of the monolayer, and $\mu$ is the exciton reduced mass, $1/\mu = 1/m_e + 1/m_h$, $m_e$ and $m_h$ being the electron and hole effective masses. As a large spin splitting of the valence bands (~0.15–0.5 eV) was predicted for monolayer TMDs [29] and also measured in optical absorption spectra [10, 30], we neglect mixing of interband transitions associated with excitons A and B, and consider only the A excitons, corresponding to the energy range of 1.8–2.0 eV of typical excitonic absorption spectra. This simpler approach has been used in previous studies [3, 23–28], and yielded exciton energy levels in agreement with experiments [13, 31].
For a TMD monolayer surrounded by media with dielectric constants \(\varepsilon_\text{a}\) (above) and \(\varepsilon_\text{b}\) (below), the effective 2D interaction can be described by the Keldysh potential [16, 17, 25, 32, 33],

\[
V(r) = \frac{\pi e^2}{2r_0} \left( H_0 \left( \frac{\varepsilon r}{r_0} \right) - Y_0 \left( \frac{\varepsilon r}{r_0} \right) \right),
\]

where \(H_0\) and \(Y_0\) are the Struve function and the Bessel function of the second kind. The length \(r_0\) relates to the 2D polarizability \(\alpha_{2D}\) of the planar material, \(r_0 = 2\pi\alpha_{2D}\), and \(\varepsilon\) is the average dielectric constant of the environment, given by \(\varepsilon = (\varepsilon_\text{a} + \varepsilon_\text{b})/2\).

As \(H\) commutes with \(L_z\), the projection of the orbital angular momentum on the \(z\) axis, \([H, L_z] = 0\), the orbital angular momentum along the \(z\) axis is conserved, and \(H\) and \(L_z\) have simultaneous eigenstates. As \(L_z\)'s eigenfunctions are \(e^{i\theta}\), \(m\) being the orbital quantum number, we write the eigenfunctions of the Hamiltonian \(H\) in a general form as

\[
\psi(r) = \frac{1}{\sqrt{2\pi}} R(r) e^{im\theta}, \quad m = 0, \pm 1, \pm 2, \ldots,
\]

which are the solutions to

\[
H\psi(r) = E\psi(r).
\]

Inserting \(H\) and the exciton wave function \(\psi(r)\) into equation (4), we find the differential equation for the radial function \(R(r)\),

\[
d^2R - \frac{1}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} V(r) R - \frac{m^2}{r^2} R = -\frac{2\mu}{\hbar^2} ER.
\]

Solving the radial equation (5) yields eigenenergy \(E\) and radial function \(R\). Quantization from equation (5) introduces additional quantum number \(n\), namely, the principal quantum number, and thus the complete form of the exciton energy \(E\) and wave function \(\psi(r)\) can be written as \(E_{nnm}\) and \(\psi_{nnm}(r) = R_{nm}(r)e^{i\theta m}/\sqrt{2\pi}\), respectively. Given \(n\) \((n = 1, 2, 3, \ldots)\), then \(|m| = 0, 1, 2, \ldots, n - 1\) [34]. Further, as \(m\) enters the RE via the term \(-m^2R/r^2\), \(E_{nm}\) and \(R_{nm}(r)\) depend only on the absolute value of \(m\), that is, \(E_{nm} = E_{n|m|}\) and \(R_{nm}(r) = R_{n|m|}(r)\), making the energy levels associated with \(\pm m\) doubly degenerate for a nonzero \(m\).

The asymptotic properties of the Bessel and Struve functions result in the 2D interaction having the following asymptotic forms:

\[
V(r) = \frac{e^2}{\varepsilon r_0} \left[ \ln \left( \frac{r}{2r_0} \right) + \gamma \right], \quad \text{for} \quad r \ll r_0, \quad (6a)
\]

\[
V(r) = \frac{e^2}{\varepsilon r}, \quad \text{for} \quad r \gg r_0, \quad (6b)
\]

where \(\gamma\) is the Euler–Mascheroni constant, \(\gamma = 0.577 215 66 \ldots\). The above expressions show that the effective 2D potential has a logarithmic divergence at very small distances while it becomes the unscreened Coulomb potential for sufficiently large distances. When \(\alpha_{2D} \to 0\) the wave functions \(\psi\) reduce to those of a 2DHM with the Coulomb potential [34],

\[
V_c(r) = \frac{e^2}{\varepsilon r},
\]

corresponding to the energies of the 2D hydrogenic Rydberg series,

\[
E_n = -\frac{\mu e^4}{2\varepsilon^2 \hbar^2 (n - 1/2)^2}, \quad n = 1, 2, 3, \ldots
\]

The Keldysh and Coulomb potentials (equations (2) and (7)) are also related through their Fourier transforms. Writing the Fourier transform of \(V_c(r)\) as \(V_c(q) = 2\pi e^2/(A\varepsilon q)\), with \(A\) being the sample area, then the Fourier transform of the Keldysh potential is given by

\[
V_q = V_{c,q}/(1 + r_0^2 q^2) = \frac{2\pi e^2}{Aq(\varepsilon + r_0q)}.
\]

Therefore the total wavevector-dependent dielectric function, including contributions of the monolayer and its surrounding media, has the form,

\[
\varepsilon(q) = \varepsilon + r_0q.
\]

This dielectric function, directly related to the Keldysh potential through equation (9), is used below in the SHM to define the effective dielectric constant (section 2.2).

The RE (5) can be transformed as

\[
r \frac{d}{dr} \frac{dR}{dr} - m^2 R + \frac{2\mu}{\hbar^2} (E r^2 - V(r) r^2) R = 0.
\]

For a small \(r\), when the asymptotic expression (6a) is used for \(V(r)\), one finds \(\lim_{r \to 0} r^2 V(r) = 0\), and the radial equation (11) reduces to

\[
r \frac{d}{dr} \frac{dR}{dr} - m^2 R = 0,
\]

yielding

\[
R(r) = Br_{nm}, \quad \text{for} \quad r \to 0, \quad (13)
\]

where \(B\) is a constant, as this form of \(R\) ensures that the wave function is finite at \(r = 0\) [35]. We note that the radial function has the same asymptotic form at the origin as that for a 2D hydrogen atom. From a general consideration of the potential energy \(-V(r)\) it is evident that the negative eigenenergies form a discrete spectrum, while the positive energies lie in the continuous spectrum. For large \(r\), we neglect the terms in \(1/r\), \(1/r^2\) and \(V(r)\) (as \(V(r) \propto 1/r\), refer to equation (6b)) of equation (5) [35] and obtain

\[
\frac{d^2 R}{dr^2} = -\frac{2\mu}{\hbar^2} ER.
\]

Then we find the asymptotic behaviour of the radial function \(R\) for large \(r\),

\[
R(r) \propto e^{-\sqrt{2\mu E}/\hbar}, \quad \text{for} \quad r \to \infty, \quad (15)
\]

which vanishes at infinity.

Introduce \(u\) by the substitution \(R = u r^2\) and scale \(r\) by a factor \(\varepsilon/r_0\), \(\rho = \varepsilon r/r_0\). Then we nondimensionalize
equation (5) and transform it after substituting expression (2) for \( V(r) \) into the following differential equation,

\[
u'' - \frac{1}{\rho} u' + \left[ \beta (H_0(\rho) - Y_0(\rho)) + \frac{1 - m^2}{\rho^2} - \lambda \right] u = 0,
\]

(16)

where the primes denote derivatives with respect to \( \rho \), \( \beta = \mu \pi e^2 r_0/(\epsilon^2 \hbar^2) \), and the eigenvalue \( \lambda \) relates to the exciton energy \( E \) via \( \lambda = -2 \mu \pi E/(\epsilon^2 \hbar^2) \), both \( \beta \) and \( \lambda \) being dimensionless.

To solve equation (16) we need the boundary conditions. From the asymptotic form of equation (13) for \( R \) in the neighbourhood of \( r = 0 \) one finds

\[ u(\rho) = C \rho^{|m|+1}, \quad \text{for } \rho \to 0, \]

(17)

where \( C \) is a constant, showing \( \lim_{\rho \to 0} u(\rho) = 0 \).

For large distances the boundary conditions are determined by \( R \)'s asymptotic form equation (15) and are given by

\[ \lim_{\rho \to \infty} u(\rho) = 0, \quad \lim_{\rho \to \infty} u'(\rho) = 0. \]

(18)

Equation (5) describes 1D motion in a semi-infinite region \((0, \infty)\). For a given \(|m|\), none of the energy levels is degenerate; there is only one eigenfunction \( R(r) \) corresponding to the eigenenergy \( E \).

To find eigensolutions the boundary value problem (equation (16)) is numerically solved using a shooting method in conjunction with fourth-order Runge–Kutta integration. A very small \( \rho \), denoted as \( \rho_0 \), and a sufficiently large \( \rho \), denoted by \( \rho_s \), are taken such that boundary condition (17) is used at \( \rho_0 \), \( u(\rho_0) = C \rho_0^{|m|+1} \); while the boundary conditions (18) are used for the \( \rho_s \) point, \( u(\rho_s) = 0, u'(\rho_s) = 0 \). The length \( \rho_s - \rho_0 \) is discretized into slices of interval \( \Delta \rho \). Beginning with the first slice, \( \rho \in [\rho_0, \Delta \rho, \rho_1] \); for an initial value of \( \lambda \), integrate inward by a Runge–Kutta method from \( \rho_s \) to \( \rho_0 - \Delta \rho \) to find the values for \( u(\rho_0 - \Delta \rho), u'(\rho_0 - \Delta \rho) \). Iterating integration over all the other intervals yields a trajectory \( u(\rho, \lambda) \) with the endpoint value of \( u(\rho_0, \lambda) \). If \( u(\rho_0, \lambda) \neq u(\rho_0) \), then by varying the \( \lambda \) value we produce trajectories until we find the trajectory which has the desired boundary value at endpoint \( \rho_0 \) and the immediate \( \lambda \) value corresponding to this trajectory is just the eigenvalue (that is related to excition energy \( E \)) for seek equation (16). The interval \( \Delta \rho \) is taken to be 0.0001. \( \rho_0 \) varies according to \( m \), while the \( \rho_s \) value varies depending on the upper bound set for the discrete exciton energies. For exciton energies lower than \(-0.05 eV\), for instance, \( \rho_s = 25.0 \) is used. Tolerances of \( 10^{-12} - 10^{-11} \) are used for \( \lambda \) to obtain accurate eigensolutions. The radial function \( R \) needs to be normalized and the normalizing constant is given by

\[ C_N = \left( \int_0^\infty R^2 r dr \right)^{-1/2} = \left( \int_0^\infty d\rho \mu^2 / \rho \right)^{-1/2}. \]

In this 1D calculation, the above numerical integration is carried out over the \( \rho \)-mesh by the trapezoidal rule.

2.2. SHM for a monolayer in a dielectric environment

The original SHM deals with a freestanding ML [3], and for a ML material on a substrate or encapsulated in a dielectric we need to extend the model to include the effects of dielectric environment by employing the dielectric function \( \varepsilon(q) \) of expression (10). An effective dielectric constant \( \varepsilon_{eff} \) is defined by averaging \( \varepsilon(q) \) in wave-vector space over a disc with radius \( 1/a_{eff} \) [3], \( a_{eff} \) being an effective radius of the exciton,

\[ \varepsilon_{eff} = \varepsilon + \frac{4\pi}{3} \alpha_{2D}/a_{eff}. \]

(19)

The exciton Bohr radius \( a_{nm} \) \((\psi_{nm} | r | \psi_{nm}) = \int R_{nm}^2 r^2 dr \) is taken as \( a_{eff} \) (\( \psi_{nm} \) is the exciton wave-function), \( a_{eff} = a_{nm} \), such that the effective dielectric constant \( \varepsilon_{eff} \) becomes dependent on \( n, m \), the exciton state, that is, \( \varepsilon_{eff} = \varepsilon_{nm} \). The exciton Bohr radius \( a_{nm} \) of the SHM [3] is assumed to equal the state-dependent Bohr radius of the 2D hydrogen atom [34] multiplied by a factor of \( \varepsilon_{nm} \).

\[ a_{nm} = \varepsilon_{nm} \mu \pi a_{nm}^2 (3n(n-1) + m^2 + 1)/(2\mu \pi). \]

(20)

Combining equations (19) and (20) then one finds \( \varepsilon_{nm} \).

\[ \varepsilon_{nm} = \frac{1}{2} \varepsilon \left( 1 + \frac{32\pi \alpha_{2D} \mu \pi}{3e^2 \hbar^2 (3n(n-1) + m^2 + 1)} \right). \]

(21)

Substituting the above expression for \( \varepsilon_{nm} \) in equation (20) gives the explicit expression for the exciton effective radius of the SHM. The exciton energy spectrum is assumed to have the form of expression (8) for the 2D hydrogenic Rydberg series, with only \( \varepsilon \) there replaced by the state-dependent effective dielectric constant \( \varepsilon_{nm} \).

\[ E_{nm} = \frac{\mu e^4}{2z^2 \varepsilon_{nm}^2} \left( \frac{1}{n+1/2} \right)^2. \]

(22)

In this study, two key parameters of monolayer TMDs, the exciton reduced mass \( \mu \) and the 2D polarizability \( \alpha_{2D} \), are needed, which are taken from [3, 24], obtained from first-principles calculations in density functional theory (DFT).

3. Results and discussions

3.1. Exciton energy spectra of a freestanding monolayer: RE solution versus SHM

We begin with a freestanding monolayer of MoS\(_2\) (\( \varepsilon_e = \varepsilon_h = 1 \)), corresponding to the suspended monolayer samples in experiments [10]. The electron and hole effective masses are taken to be 0.5 \( m_0 \) (\( m_0 \) is the electron rest mass), giving the exciton reduced mass \( \mu = 0.25 \mu_0 \). We use the 2D polarizability 6.6 \( \AA \) [24], corresponding to a screening length \( r_0 = 41.5 \) \( \AA \).

Figure 1 shows eight Rydberg series of exciton energy levels for \( E_{nm} \) up to \(-0.04 eV\), corresponding to eight orbital quantum number \(|m| = 0-7\), calculated from the RE. The ground state, \( n = 1 \), \( m = 0 \), which is denoted by 1s following conventional notation for the 2D hydrogen atom [3, 6, 14, 34], has a binding energy 0.555 eV that is very close to the value 0.54 eV calculated using the same parameters [24]. Above the 1s state is the doubly degenerate 2p exciton states of \( n = 2, m = \pm 1 \), followed by the 2s state, \( n = 2, m = 0 \). We also see quasicontinuum states above a series of discrete exciton levels. Compared to the 2D hydrogenic Rydberg series (expression (8)), the exciton energy levels are elevated.
having smaller magnitudes; for the ground state, for instance, the 2DHM yields an energy of $-13.6\,\text{eV}$ with reduced mass $\mu = m_0/4$, far lower than the $-0.555\,\text{eV}$ energy. Neglecting screening due to the monolayer ($\alpha_{2D} = 0$), the Keldysh interaction (equation (2)) becomes simply the 2D Coulomb potential (equation (7)). The difference between the exciton energy spectrum (figure 1) and the hydrogenic Rydberg series is thus entirely due to the 2D dielectric screening, which has weakened the electron–hole Coulomb attraction and thus reduced the exciton binding energies while raising the exciton energies.

With an $e–\hbar$ Coulomb interaction, as expression (8) shows, all exciton states with different $m$ but the same $n$ have the same energy (i.e. the Coulomb degeneracy); now we see from figure 1 that this degeneracy of exciton levels is lifted as the Keldysh interaction in ML MoS$_2$ deviates significantly from the Coulomb potential. For the same $n$, the principal quantum number, the energy level of $E_{n|m}$ is lower for a larger $|m|$, a phenomenon that has been found in a previous study using a first-principles GW-BSE approach [6]. This result indicates that the 2D dielectric screening associated with exciton $(n,m)$ becomes weaker as $|m|$ increases (for a fixed $n$). To explain this we look at the effective Bohr radius of exciton $(n,m)$. The effective Bohr radii of six strongly bound exciton states are given in figure 1, bracketed just below the exciton energy levels (values in Å). The 2D excitons are of Wannier type as their effective radii are much larger than the unit cell dimensions (the lattice constant of monolayer MoS$_2$ is 3.16 Å). Our calculation shows that the exciton Bohr orbit shrinks as $|m|$ gets larger for the same $n$. A Bohr orbit of shorter radius $\alpha_{nm}$ corresponds to a stronger electron–hole interaction and weaker dielectric screening, according to equation (2), thus giving rise to a larger exciton binding energy. Furthermore, as angular momentum $L_z$ is conserved, its eigenvalue being $m\hbar$ in exciton state $\psi_{nm}$, we write $|m|\hbar = \mu \omega_{nm} \alpha_{nm}$, where $\omega_{nm}$ is the orbital frequency (circular). Evidently a greater angular momentum $|m|\hbar$ together with a shorter exciton Bohr radius $\alpha_{nm}$ leads to a larger frequency $\omega_{nm}$ or shorter orbital period for the exciton, a further result from the reduced dielectric screening.

The energy levels get closer to those of the 2DHM (equation (8)) as $n$ increases (for instance, for the 8s exciton $n = 8$, $m = 0$, its energy $-0.037\,\text{eV}$, is only 0.02 eV higher than the energy $E_0$ given by equation (8)), because at a larger distance $r$ (or equally, a larger exciton Bohr radius $\alpha_{nm}$) the Keldysh interaction approaches more closely the 2D Coulomb potential. The number of nodes of the radial functions $R_{nm}(r)$ follows that of a 2D hydrogen atom, $n - |m| - 1$, as is illustrated in figure 2 for the $R_{nm}(r)$ of the six low-energy levels, 1s, 2s, 2p, 3s, 3p, 3d.

In figures 3(a)–(c) we show the exciton Rydberg series by the absolute values of the energies for $|m| = 0, 1, 2$, respectively, calculated with the SHM (equations (21) and (22)) and from the RE (5). We see that the exciton energies evaluated with the SHM are in good agreement with our numerical calculation except that the binding energies of the 1s, 2p, 3d excitons, i.e. the most strongly bound excitons, are underestimated by 23%, 32%, 30%, respectively. Such a discrepancy in exciton energy can be explained as follows. In the SHM, the averaging over $q$ to obtain the effective screening $\varepsilon_{\text{eff}}$ (expression (19)) is carried out for only long wavelengths, $\lambda > a_{\text{eff}}$, and the shorter wavelengths (larger-$q$) contribution may become appreciable for excitons with a small radius or equally a large binding energy. In addition, the energy expression (22) has a form taking from the 2D hydrogenic Rydberg series (expression (8)), a result from the 2D Coulomb potential, and is only an effective approach when dealing with excited states with a large exciton radius. The exciton energy discrepancies above correspond to the overestimates of the 2D dielectric screening by 14%, 21%, 20% for excitons 1s, 2p, 3d.
respectively, which also explains the sharp rise of the effective dielectric constant $\varepsilon_{nm}$ occurring on the small $n$ side for $|m| = 0, 1, 2$, as shown in the insets of figure 3. For the ground states of the freestanding ML TMDs, the SHM was analyzed based on a comparison with the effective mass (see figure 1 of [3]) or first-principles BSE (see figure 26 of [21]) calculations, and both studies [3, 21] found an underestimate with the SHM of the exciton binding energies. In [3], for instance, the exciton binding energy of freestanding ML MoS2 was found to be underestimated by 11% with the SHM, smaller than the 23% underestimate we calculated, as they used a larger exciton effective mass and smaller 2D polarizability, $\mu = 0.276 m_0$ and $\alpha_{2D} = 5.83 \text{Å}$. The exciton effective radius $a_{nm}$ is a key parameter of the SHM, and $a_{nm}$ versus $n$ for $|m| = 0, 1, 2$ are shown in figure 4(b); comparing with the RE result (figure 4(a)) we see that the SHM has captured the main character of the radius $a_{nm}$'s dependence on $n$. According to equation (20), the effective radius $a_{nm}$ of the SHM is equal to the product of the effective dielectric constant $\varepsilon_{nm}$, which decreases as $n$ becomes larger (equation (21)), and the Bohr radius of the 2DHM, $a_{nm}^{\text{2DHM}} = \frac{\hbar}{\sqrt{2\varepsilon_{nm} m_0^2 \alpha_{2D}}}$, which increases with $n$. Inserting equations (21) into (20) finds immediately that the effective radius $a_{nm}$ increases with $n$.

Now we look at how the energies of the exciton energy spectrum vary quantitatively with the orbital quantum number $m$. Our RE solution shows that for a given $n$, the principle quantum number, the exciton binding energy $|E_{nm}|$ increases with the orbital quantum number $m$ (figure 5(a)), and further the increase is linear, with a slope that decreases as $n$ becomes larger. In contrast, the SHM yields very different results (figure 5(b)), which predicts that the energy $|E_{nm}|$ decreases as $m$ increases, in a nonlinear manner. For a given $n$, the effective dielectric constant $\varepsilon_{nm}$ increases very slowly as $m$ gets larger (not shown), and therefore the SHM’s effective radius varies with $m$ (figure 6(b)) in a manner very similar to that of the 2DHM (figure 6(c)) which is dictated by a quadratic $-m^2$ dependence (refer to expression (20)), the difference being simply that the SHM yields a slightly larger effective radius after accounting for the dielectric screening (comparing figures 6(b) and (c)). On the other hand, the exciton effective radius $a_{nm}$ of the SHM varies with $m$ (figure 6(b)) in a manner that is very different from the result calculated from the RE in figure 6(a), which displays a linear $m$-dependence with the
slope remaining almost unchanged as \( n \) varies. As a result, the SHM has failed to describe the variation of the exciton energy \( E_{nm} \) with orbital quantum number \( m \) of the exciton energy spectrum.

### 3.2. 2D excitonic variational wave functions

The 2D excitons due to the usual \( e^-h \) Coulomb interaction can be described analytically with a 2DHM [1, 36], in which the wave function of the ground state is

\[
\phi_{10}(\mathbf{r}) = \sqrt{\frac{2}{\pi a_0^2}} e^{-r/a_0},
\]

and the first excited states are triply degenerate,

\[
\phi_{2\pm1}(\mathbf{r}) = \frac{4}{\sqrt{3\pi a_0^2}} e^{-2r/3a_0} e^{\pm i\theta},
\]

where \( a_0 \) is the exciton Bohr radius, \( a_0 = \hbar^2 \varepsilon/(\mu e^2) \), \( \varepsilon \) being the dielectric constant of the material. For excitons in monolayer TMDs that have an effective interaction as given by expression (2), analytical expressions will be very useful for practical calculations of the 2D exciton properties such as the binding energies, internal exciton transitions (e.g. \( 1s - 2p \) or \( 2s - 2p \) transition induced by an external electric field [37]) and Stark effects (as is demonstrated in section 3.4 below). Considering that the numerically calculated wave functions have a nodal structure (figure 2) similar to that of the 2D hydrogenic wave-functions, we construct variational wave functions \( \phi_{nm}(\mathbf{r}) \) in the following forms for the first three energy levels,

\[
\phi_{10}(\mathbf{r}) = \sqrt{\frac{2}{\pi a^2}} e^{-r/a}, \quad (23a)
\]

\[
\phi_{2\pm1}(\mathbf{r}) = \frac{2r}{\sqrt{3\pi a'^2}} e^{-r/a'} e^{\pm i\theta}, \quad (23b)
\]

\[
\phi_{20}(\mathbf{r}) = \frac{4}{\sqrt{3\pi a'^2}} \left[ \frac{1}{2} \left( 1 + \frac{a'}{a} \right) \frac{r}{a'} - 1 \right] e^{-r/a'}, \quad (23c)
\]
where $a$, $a'$, $a''$ are the variational parameters, and $\eta$ is dimensionless, introduced for normalization, $\eta = \eta = (a''/a)^2 - \frac{2}{3}a''/a + 1$. These trial wave functions $\phi_{nm}(r)$ have similar forms to the hydrogenic wave functions $\varphi_{nm}(r)$ above, and further they are orthogonal and normalized.

To calculate the expectation values of $H$, namely, $E_{10}(a) = \langle \phi_{10} | H | \phi_{10} \rangle$, $E_{2\pm 1}(a') = \langle \phi_{2\pm 1} | H | \phi_{2\pm 1} \rangle$, $E_{20}(a'') = \langle \phi_{20} | H | \phi_{20} \rangle$, which involve integrals over $r = (r, \theta)$, we expand the Keldysh potential $V(r)$ (equation (2)), $V(r) = \sum_q V_q e^{i q \cdot r}$, where $V_q$ is given by equation (9), such that the integration over $r, \varphi$ is also obtained analytically after converting the summation over $q$ to a double integral. After a lengthy derivation then we obtain for the expectation values the following expressions,

$$E_{10}(a) = \frac{\hbar^2}{2 \mu a^2} - \frac{2e^2}{\varepsilon a} P_0 \left( \frac{2r_0}{\varepsilon a} \right),$$

$$E_{2\pm 1}(a') = \frac{\hbar^2}{2 \mu a^2} + \frac{e^2}{\varepsilon a} \left[ 3P_1 \left( \frac{2r_0}{\varepsilon a} \right) - 5P_2 \left( \frac{2r_0}{\varepsilon a} \right) \right],$$

$$E_{20}(a'',a) = \frac{8}{\eta} \left\{ \left( 1 + \frac{1}{\nu} \right) \frac{\hbar^2}{3 \mu a^2} + \frac{2e^2}{3 \varepsilon a^3} \left[ (2

where $\nu = \frac{1}{4}(1 + a''/a)$, and the dimensionless functions $P_0(x), P_1(x), P_2(x)$ are given by

$$P_0(x) = \frac{x^2}{1 + x^2} \left\{ \frac{1 - x}{x^2} + (1 + x)^{1/2} \left[ \sinh^{-1}(x) + \sinh^{-1} \left( \frac{1}{x} \right) \right] \right\},$$

$$P_1(x) = \frac{x^2}{1 + x^2} \left[ \frac{2 - x}{3x^2} + P_0(x) \right],$$

$$P_2(x) = \frac{x^2}{1 + x^2} \left[ \frac{8 - 3x}{15x^2} + P_1(x) \right],$$

and $\sinh^{-1}(x)$ being the inverse hyperbolic sine, $\sinh^{-1}(x) = \ln(x + \sqrt{x^2 + 1})$. We have checked and verified these expressions by comparing their values with those $H$’s expectation values that are obtained by numerically integrating $\langle \psi_{nm} | V | \psi_{nm} \rangle$, with expression (2) for $V(r)$, using a Gauss–Legendre quadrature method. The energy expressions for the higher-energy levels such as $E_{20}$ become more complicated as more variational parameters are needed in the orthogonalization of the wave functions.

Continuing with freestanding monolayer MoS$_2$, we plot the expectation values of $E_{10}$ and $E_{2\pm 1}$ as functions of variational parameters $a$ and $a'$, respectively, in figures 7(a) and (b). From these one finds the minimum of $E_{10}$ at $a = 10.4$ Å and the minimum of $E_{2\pm 1}$ at $a' = 11.2$ Å, yielding the 1s and 2p exciton energies $E_{10} = -0.543$ eV, and $E_{2\pm 1} = -0.312$ eV. Having the $a$ value, one then plots the $E_{20}$ versus $a''$ curve (figure 7(c)) that gives the 2s exciton energy $E_{20} = -0.242$ eV with $a'' = 16.1$ Å. These exciton energies are very close to the RE solutions above, the former being larger by 2%, 2%,
6% for the 1s, 2p, 2s exciton, respectively. Furthermore, the wave-functions obtained from the VM and RE solution are very close, as shown in figure 8.

We calculated the exciton energy spectra of monolayer MoS2 on various substrates by solving the RE (5), with an average background dielectric constant \( \varepsilon = \frac{(1 + \varepsilon_s)}{2} \). To further check the VM (equations (24a)–(24c)) and SHM in strongly bound exciton calculation, we compared the results of the two methods with the RE calculation for the 1s, 2p, 2s excitons (table 1). The SHM yields a 1s exciton binding energy \( |E_{10}| \) which is 20% lower for a freestanding monolayer and 10% lower for monolayer MoS2 on substrate SiO2 (with a smaller \( \varepsilon_s \)), but ~9% higher for monolayer MoS2 on substrate hBN or diamond (with a larger \( \varepsilon_s \)). For the 2s and 2p excitons, the SHM predicts \( |E_{20}| > |E_{21}| \), which is different from the RE result, \( |E_{20}| < |E_{21}| \), consistent with the above finding from figure 5. The VM and RE solution again yield very close exciton energies, with the 2s energies having the largest deviation of 6%.

3.3. Exciton energy spectra of a supported monolayer: RE solution, SHM and experiment

The s exciton states were probed in measurements of the linear optical spectra of monolayer WS2 on a SiO2 substrate [13], and the result was also reproduced well with an effective mass calculation using the Keldysh electron–hole interaction [13]. Here in figure 9(a) we show the exciton energy spectrum \( E_{nm} \) for monolayer WS2 on the SiO2 substrate (\( \varepsilon_s = 2.1 \), see the supplemental material of [13]) consisting of the s (\( m = 0 \)), p (\( m = 1 \)), d (\( m = 2 \)) excitons, calculated from the RE using the reduced mass and 2D polarizability \( \mu = 0.22m_0 \) and \( \alpha_{2D} = 6.35 \text{ Å} \) as obtained from DFT calculations in the supplemental material of [3]. The 1s, 2p, 2s excitons remain deeply confined, and their energies are very close to those of our variational calculations (solid squares in figure 9(a)). The binding energies are significantly reduced due to the additional screening from the substrate, and the excitons with energies above the 5s state approach the quasi-continuum states. Interestingly, we see again that for the same principle quantum number \( n \) excitons with a larger orbital quantum number \( m \) have a lower energy and accordingly a larger binding energy, for instance, \( E_{32} < E_{31} < E_{30} \). Furthermore, for a given \( n \), the exciton energy \( E_{nm} \) and effective radius \( a_{nm} \) both display a linear decrease with \( m \), as is
Exciton energy. DFT calculations of [3] were used in our calculation. The 2DHM yields a 1s exciton state, calculated from the radial equation (VM) (expressions (24c)–(24e)) for excitons 1s, 2p, 2s (solid squares), and (b) the s (m = 0) exciton states, calculated from the radial equation (RE) (5), the screened hydrogen model (SHM) and 2D hydrogen model (2DHM) (expression (8)) and obtained from the reflectance contrast measurements in the experimental study [13]. Reduced mass equation (RE) (5), the screened hydrogen model (SHM) and 2D hydrogen model (2DHM) (expression (8)) and obtained from the

\[ \alpha_{\text{2D}} = 6.35 \AA \]

from DFT calculations of [3] were used in our calculation. The 2DHM yields a 1s exciton energy ~−5 eV that is too low to be shown in (b).

Table 1. Comparison of exciton binding energies of the ground state 1s and the first and second excited states 2p and 2s, calculated with the variational method (VM) (equations (24c)–(24e)) and from the solution of the radial equation (5), for freestanding monolayer MoS2 and monolayer MoS2 on three different substrates SiO2, hBN or diamond with background dielectric constant \( \varepsilon = (1 + \varepsilon_s)/2 \).

| Substrate | \( \varepsilon \) | \(|E_{1s}\)| | \(|E_{2p}\)| | \(|E_{2s}\)| |
|-----------|-----------------|-----------------|-----------------|-----------------|
|            | RE  | VM  | SHM | RE  | VM  | SHM | RE  | VM  | SHM |
| Vacuum     | 1.00 | 0.555 | 0.543 | 0.428 | 0.318 | 0.312 | 0.216 | 0.258 | 0.242 | 0.243 |
| SiO2       | 1.55 | 0.431 | 0.422 | 0.385 | 0.217 | 0.214 | 0.168 | 0.172 | 0.161 | 0.185 |
| hBN        | 3.00 | 0.269 | 0.263 | 0.292 | 0.105 | 0.103 | 0.091 | 0.080 | 0.076 | 0.097 |
| Diamond    | 3.35 | 0.246 | 0.240 | 0.273 | 0.089 | 0.089 | 0.080 | 0.070 | 0.066 | 0.084 |

Figure 9. Exciton Rydberg series \( E_{nm} \) versus principle quantum number \( n \) of monolayer WS2 on the SiO2 substrate (\( \varepsilon_s = 2.1 \)) for (a) the s (\( m = 0 \)), p (\( m = 1 \)), d (\( m = 2 \)) exciton states, calculated from the radial equation (RE) (5) and also with the variational method (VM) (expressions (24c)–(24e)) for excitons 1s, 2p, 2s (solid squares), and (b) the s (\( m = 0 \)) exciton states, calculated from the radial equation (RE) (5), the screened hydrogen model (SHM) and 2D hydrogen model (2DHM) (expression (8)) and obtained from the reflectance contrast measurements in the experimental study [13]. Reduced mass \( \mu = 0.22m_0 \) and 2D polarizability \( \alpha_{\text{2D}} = 6.35 \AA \) from DFT calculations of [3] were used in our calculation. The 2DHM yields a 1s exciton energy ~−5 eV that is too low to be shown in (b).

shown in figures 10(a) and (b), respectively, similar to the freestanding monolayer case above. Again the group of \( a_{nm} \) versus \( m \) lines displays almost a single slope.

The experimental data of s excitons of [13] are added to figure 9(b) (solid circles) to make a quantitative comparison with our RE calculation (diamonds) and also the results of the SHM (triangles) and 2DHM (stars). In particular we note that the original SHM of Olsen et al [3] has been extended to account for screening due to the substrate, thus allowing for such a direct comparison of the SHM result with experiment. Our calculated exciton energies are in good agreement with experiment except for the 1s energy, which is ~0.09 eV lower than the experimental value, similar to the discrepancy 0.08 eV given in the supplemental material of [13]). The SHM overestimates the 1s exciton binding energy by 0.06 eV with respect to its experimental value. Despite this, overall it yields exciton energies close to both our RE calculation and the experimental data, thus making a good prediction for the non-hydrogenic behaviour of the s exciton Rydberg series. In contrast, the 2DHM (expression (8)) yields much larger exciton binding energies, in particular for the low-lying exciton states, as has been noted in [13]; for instance, the 2DHM ground state binding energy 5 eV is more than one order of magnitude larger than the experimental value 0.32 eV.

Unlike the s states, the p states are excitonic dark states as they do not appear in the linear optical spectrum. In another experimental study [6], both s and p exciton energy levels were measured for monolayer WS2 on substrate SiO2, and in particular the p exciton states were probed using two-photon excitation spectroscopy. In the measured spectrum of p excitons (figure 2 of [6]), there are two broad features of spectral widths 0.11 and 0.07 eV, respectively, peaking at energies 0.24 and 0.43 eV, respectively, above the 1s state. In fact our calculated 1s − 2p separation 0.22 eV is very close to the experimental value of 0.24 eV; further the 1s − 3p energy interval we calculated, 0.3 eV, suggests that the 3p excitons may contribute to the lower-energy absorption feature while broadening its energy range. The higher-energy feature can be attributed to the absorption due to 4p, 5p, 6p excitons, which appear energetically 0.37–0.41 eV higher than the 1s state (figure 9(a)).

The exciton ground state energies of freely suspended ML TMDs and ML TMDs on a SiO2 or hBN substrate have been calculated in previous studies using various approaches, with
more calculations performed for suspended monolayers. We also calculated the ground state exciton binding energies for TMD monolayers in different dielectric environments (table 2 of [38]), using the exciton reduced mass and 2D polarizability values from the DFT calculations of [3] (supplemental material therein). The binding energies we calculated are very consistent with experimental results, as discussed in [38].

3.4. Stark effects

We now turn to the 2D excitons in an applied in-plane electric field \( F \). Then the eigenequation is given by \((H + eF \cdot r)\Psi(r) = E\Psi(r)\), where \( H \) is the Hamiltonian in the absence of an electric field (equation (1)). We confine ourselves to the strongly bound low-energy excitons of 1s, 2p, 2s (constituting a four-state model system), which dominate the exciton absorption spectrum in the low energy region [6, 13, 14, 31]. The variational wave-functions at zero field (equations (23a)–(23c)) that we constructed above can now be used conveniently to study the Stark effects in monolayer TMDs.

As the 1s and 2s wavefunctions are even and the 2p wavefunction is odd in parity, the electric field couples the exciton states 1s and 2p as well as exciton states 2s and 2p, and therefore only matrix elements \( \langle \phi_{2s} | eF \cdot r | \phi_{20} \rangle \) and \( \langle \phi_{2±s} | eF \cdot r | \phi_{10} \rangle \) are nonzero. Letting \( F \) along the x axis, one finds

\[
V_1 = \langle \phi_{2±s} | eFx | \phi_{10} \rangle = eFa4 \sqrt{6a} a'^2/(a + a')^4,
\]

\[
V_2 = \langle \phi_{2±s} | eFx | \phi_{20} \rangle = eFa'^4 6a^2 a''^2/(a' + a'')^4 [2(1 + a''/a') a''/(a' + a'')] - 1/\sqrt{7}.
\]

Given a field strength \( F \), the exciton energies are solutions to the secular equation,

\[
(E - E_{21}) \left\{ E^3 - (E_{10} + E_{21} + E_{20}) E^2 + [E_{10} E_{21} + E_{21} E_{20} + E_{10} E_{20} - (2V_1^2 + V_2^2)] E + (2V_1^2 E_{10} + 2V_1^2 E_{20} - E_{10} E_{20}) \right\} = 0,
\]

which are shown in figures 11(a) and (b) for the ground state (1s) and the excited states (2p and 2s) in freestanding monolayer MoS\(_2\). With an electric field applied, clearly the 1s energy level is redshifted while the 2p level splits into two.

Using second-order perturbation theory, we obtain an analytical expression for the energy shift of the ground state, \( \delta E_{10} = -\alpha F^2/2 \), i.e. the second-order Stark effect, where \( \alpha \) is the electric polarizability of the exciton [32, 33], given by

\[
\alpha = 384 e a^2/(E_{21} - E_{10}) (a a')^4/(a + a')^8.
\]

This quadratic dependence of \( E_{10} \) on the field \( F \) is also plotted in figure 11(a) (dotted curve), showing the perturbative approach yields an accurate correction to the ground state energy for fields below 50 V \( \mu \text{m\textsuperscript{-1}} \). The electric polarizability of the ground state exciton is \( \alpha = 7 \times 10^{-18} \text{eV(m V\textsuperscript{-1})}^2 \); its energy redshift is 1.4 meV at \( F = 20 \text{V \mu m\textsuperscript{-1}} \), and increases to 9 meV at \( F = 50 \text{V \mu m\textsuperscript{-1}} \), close to the energy shifts of 1.5 and 10 meV for the two field strengths respectively that were reported in [33]. For monolayer MoS\(_2\) on the SiO\(_2\) substrate (average dielectric constant \( \varepsilon \) is taken to be 2.45, the same as in [33] for comparison of the exciton energies), the polarizability of the ground state exciton increases to 1.1 \times 10^{-17} \text{eV(m V\textsuperscript{-1})}^2 \), corresponding to an energy redshift of 2.3 meV at \( F = 20 \text{V \mu m\textsuperscript{-1}} \), close to the 3 meV redshift in [33]. For monolayer MoS\(_2\) encapsulated in h-BN (average dielectric constant \( \varepsilon = (5 + 5)/2 = 5 \)), we find
1.4 \times \text{an exciton effective radius and effective dielectric constant as in the SHM, an improved version of the 2DHM, which uses subsequently the exciton binding energy to be raised. We examined the SHM, an improved version of the 2DHM, which uses}

- causes the electron-hole interaction to be enhanced and consequently the exciton Bohr orbit which decreases linearly as \(m\) increases, and the energy decrease is due to the shrink of the exciton Bohr orbit which causes the electron-hole interaction to be enhanced and consequently the exciton binding energy to be raised. We examined the SHM, an improved version of the 2DHM, which uses an exciton effective radius and effective dielectric constant as key parameters, by comparing its exciton energy spectra with the RE calculations. The SHM described the exciton Rydberg series reasonably well. For a given \(n\), however the SHM failed to account for the dependence of the exciton energy on the orbital quantum number \(m\). The exciton effective radius expression (20), generalized from the 2DHM, can characterize the exciton radius’s dependence on \(n\), but it cannot properly describe the exciton radius’s dependence on \(m\), which is the cause of the SHM’s poor description of the \(m\)-dependence of the exciton energy.

The simpler approach above yields splitting of the 2\(p\) states, and also offers an accurate description of the ground state and its energy shift. This is largely because the 1\(s\) and 2\(p\) states are strongly bound states and the high energy levels above make a very small contribution. For a more accurate description of the Stark effects, one of course needs to account for these high energy states in further study.

4. Conclusions

In conclusion, we have studied 2D exciton energy spectra of monolayer TMDs with an effective mass model using the Keldysh potential for the screened electron-hole interaction. Freestanding monolayer TMDs as well as monolayers on various substrates have been considered. The excitonic Schrödinger equation is reduced to a 1D RE, and the boundary conditions for the exciton radial functions are obtained after considering the asymptotic expressions of the Keldysh potential. The exciton states are numerically calculated by solving the RE with a shooting method including fourth-order Runge–Kutta integration. The RE results showed that the exciton energy decreases linearly as \(m\) increases, and the energy decrease is due to the shrink of the exciton Bohr orbit which causes the electron-hole interaction to be enhanced and consequently the exciton binding energy to be raised. We examined the SHM, an improved version of the 2DHM, which uses an exciton effective radius and effective dielectric constant as key parameters, by comparing its exciton energy spectra with the RE calculations. The SHM described the exciton Rydberg series reasonably well. For a given \(n\), however the SHM failed to account for the dependence of the exciton energy on the orbital quantum number \(m\). The exciton effective radius expression (20), generalized from the 2DHM, can characterize the exciton radius’s dependence on \(n\), but it cannot properly describe the exciton radius’s dependence on \(m\), which is the cause of the SHM’s poor description of the \(m\)-dependence of the exciton energy.

We also paid attention to two experimental studies on exciton energy levels, one measuring \(s\) excitons while the other probing both \(s\) and \(p\) excitons, for monolayer WS\(_2\) on substrate SiO\(_2\). The measured \(s\) exciton Rydberg series provided us with a double check of both the SHM and RE solution. We also analyzed the two-photon absorption spectrum, and explained its two broad features in terms of the dark \(p\) excitons: the lower-energy feature arises due to both 2\(p\) and 3\(p\) exciton absorption whereas the higher-energy feature is attributed to the absorption due to the higher energy \(p\) excitons.

Based on the RE solutions, we constructed variational wave functions with the 2D hydrogenic wave functions for the three lowest exciton energy levels, 1\(s\), 2\(p\), 2\(s\), and also verified their accuracy for exciton calculation by checking the energies and wave functions against the RE results. Further we demonstrated an application of these analytical wave-functions by using them to study the Stark effects for a monolayer TMD in an in-plane electric field. We found that the ground state energy is redshifted while the 2\(p\) level is split into two. We derived an analytical expression for the ground state energy shift, quadratically dependent on the field due to the second-order Stark effect, which can be conveniently used to calculate the redshift to a good accuracy. The numerical solution of the RE combined with the VM provides a simple and effective approach for the study of 2D excitons in monolayer TMDs.
Acknowledgments

We acknowledge support from the Natural Science Research Funds (No. 419080500175) of Jilin University.

ORCID iDs

J-Z Zhang https://orcid.org/0000-0002-0757-4184

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