Trion and Biexciton in Monolayer Transition Metal Dichalcogenides

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We study the trion and biexciton in transition metal dichalcogenides monolayers within the framework of a nonrelativistic potential model using the method of hyperspherical harmonics (HH). We solve the three- and four-body Schrödinger equations with the Keldysh potential by expanding the wave functions of a trion and biexciton in terms of the antisymmetrized HH. Results of the calculations for the ground state energies are in good agreement with similar calculations for the Keldysh potential and in reasonable agreement with experimental measurements of trion and biexciton binding energies.

I. INTRODUCTION

Monolayer transition metal dichalcogenides (TMDCs) are a new class of two-dimensional (2D) materials with remarkable optical and electronic properties. The TMDC family includes MoS2, MoSe2, WS2 and WSe2, all of which share similar properties with respect to atomic and electronic structure. Unlike graphene, these 2D crystals are believed to be direct band gap semiconductors. A result of reduced dimensionality and weak dielectric screening in such materials is a strong electrostatic interaction allowing the formation of bound state complexes of electrons and holes with very large binding energies. The latter phenomenon is remarkably pronounced in monolayer TMDCs, leading to the formation of tightly bound excitons with binding energies of several hundred millielectronvolts. An observed consequence of reduced dimensionality and weak dielectric screening in such materials is a strong electrostatic interaction allowing the existence of other stable bound states consisting of a larger number of electrons and holes, such as positively or negatively charged trions (X±) and biexcitons. In TMDC monolayers, X± is formed by an exciton with an extra hole or electron, which can be introduced in different ways. The trion binding energies extracted from recent experimental observations such as photoluminescence, electroluminescence, and absorption spectroscopy in monolayer TMDCs were found to be in the range of 10-43 meV [1–10]. Very recent evidence of stable bound states of two electrons and two holes—biexcitons—with binding energies of ∼20–70 meV in TMDCs has been reported in Refs. [4, 5, 11–14].

Until now several approaches have been proposed for evaluating the binding energies of exciton complexes such as trion and biexciton in two-dimensional transition metal dichalcogenides. Initial work on exciton and trion binding energies in TMDCs employed variational wave functions [15], and more recently used more intricate trial wave functions [13, 16]. Exciton complexes in low dimensional TMDCs studied using the time-dependent density-matrix functional theory [17], the stochastic variational method using the explicitly correlated Gaussian basis [18, 19]. Within the effective mass approach, quantum Monte Carlo methods, such as the diffusion Monte Carlo and the path integral Monte Carlo, provide accurate and powerful means for studying few-particle systems. Trions and biexcitons in 2D TMDC sheets of MoS2, MoSe2, WS2, and WSe2 are studied by means of the density functional theory and path integral Monte Carlo method in [20], the path integral Monte Carlo methodology in [21], and the diffusion Monte Carlo approach in [22].

In this work we study the trion and biexciton in TMDC monolayers in the effective mass approximation within the framework of a nonrelativistic potential model using the method of hyperspherical harmonics (HH). For the solution of three- and four-body Schrödinger equations with the Keldysh potential [23], we expand the wave functions of three- and four bound particles in terms of the antisymmetrized hyperspherical harmonics, and obtain the corresponding hyperradial equations that are solved numerically.

II. THEORETICAL MODEL

Within the effective mass approximation, the nonrelativistic Hamiltonian of an excitonic few-particle system lying in a 2D plane is

\[
H = -\frac{\hbar^2}{2}\sum_{i=1}^{N} \frac{1}{m_i}\nabla_i^2 + \sum_{i<j}^{N} V_{ij}(|r_i - r_j|),
\]  (1)
where \( m_i \) and \( \mathbf{r}_i \) are the effective mass and the \( i \)th particle position, respectively. We assume only two types of charge carriers: electrons and holes with the corresponding effective masses. Below we restrict ourselves to \( N = 3 \) (trion) and \( N = 4 \) (biexciton). The screened Coulomb interaction \( V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) \) between \( q_i \) and \( q_j \) charges in Eq. (11) for monolayer TMDCs was derived by Keldysh [23]:

\[
V_{ij}(r) = \frac{\pi q_i q_j}{\rho_0} \left[ \frac{H_0(r/\rho_0)}{\rho_0} - \frac{Y_0(r/\rho_0)}{\rho_0} \right].
\]

In Eq. (2) \( H_0(\frac{r}{\rho_0}) \) and \( Y_0(\frac{r}{\rho_0}) \) are the Struve function and Bessel function of the second kind, respectively, \( \rho_0 \) is the screening length \( \rho_0 = 2\pi \chi \), where \( \chi \) is the polarizability of the 2D materials, which sets the boundary between two different behaviors of the potential due to a nonlocal macroscopic screening. For large distances \( r \gg \rho_0 \) the potential has the three-dimensional Coulomb tail, while at very small \( r \ll \rho_0 \) distances it becomes a logarithmic Coulomb potential of a point charge in two dimensions.

To obtain a solution of the Schrödinger equations for the trion and biexciton using the Hamiltonian (1), we use the method of hyperspherical harmonics. The main idea of this method is the expansion of the wave function of the corresponding excited states in terms of \( \text{HH} \) that are the eigenfunctions of the angular part of the Laplace operator in the four-dimensional (4D) space (trion) or in the six-dimensional (6D) space (biexciton). As the first step by introduction of the trees of Jacobi coordinates for a trion or biexciton and considering that the electron and hole have unequal masses one can separate the center-of-mass and write the nonrelativistic Schrödinger equation for the relative motion of \( N \) particles. Below we restrict ourselves to \( N \) bound particles in terms of the \( \text{HH} \) one obtains

\[
\Psi(\rho, \Omega_{\rho}) = \rho^{-\frac{2N-3}{2}} \sum_{\mu, \lambda} u_{\mu}^\lambda(\rho) \Phi_{\mu}^\lambda(\Omega_{\rho}, \sigma),
\]

where \( \Phi_{\mu}^\lambda(\Omega_{\rho}, \sigma) \) are fully antisymmetrized functions with respect to two electrons in the case of the negative trion and two electrons and two holes in the case of the biexciton. These functions are constructed from spin function and the hyperspherical harmonics. The \( \text{HH} \) are the eigenfunctions of the angular part of the \( 2(N-1) \)-dimensional Laplace operator in configuration space with eigenvalue \( L_N(L_N + 1) \), where \( L_N = \mu + (2N - 5)/2 \). They are expressible in terms of spherical harmonics and Jacobi polynomials [24, 25]. In Eq. (3), for the sake of simplicity, we denote by \( \lambda \) the totality of quantum numbers on which the \( N \)-body hyperspherical harmonics depend and the integer \( \mu \) is the global momentum in the \( 2(N-1) \)-dimensional configuration space, which is the analog of angular momentum in the case of the exciton, \( N = 2 \). Introducing the expansion (3) in the Schrödinger equation for \( N \)-bounded particles one can separate the radial and angular variables that results in a system of coupled differential equations for the hyperradial functions \( u_{\mu}^\lambda(\rho) \)

\[
\frac{d^2 u_{\mu}^\lambda(\rho)}{d \rho^2} + \left[ \kappa^2 - \frac{L_N(L_N + 1)}{\rho^2} \right] u_{\mu}^\lambda(\rho) = \sum_{\mu', \lambda'} V_{\mu \mu'} \lambda' \lambda' (\rho) u_{\mu'}^{\lambda'}(\rho),
\]

where

\[
V_{\mu \mu'} \lambda' \lambda' (\rho) = \frac{2M}{\hbar^2} \int \left[ \Phi_{\mu}^\lambda(\Omega_{\rho}, \sigma) \right]^* \left( \sum_{i<j} V_{ij} \right) \Phi_{\mu'}^{\lambda'}(\Omega_{\rho}, \sigma) d\Omega_{\rho}
\]

is the \( N \)-particle effective potential energy defined by the Keldysh potential \( V_{ij} \) [2], \( \kappa^2 = 2MB/\hbar^2 \), where \( B \) is the binding energy, and \( M \) is a reduced mass for trion or biexciton.

### III. RESULTS OF CALCULATIONS

The system of coupled differential equations (4) for the hyperradial functions \( u_{\mu}^\lambda(\rho) \) is infinite and the corresponding hyperradial equations are solved numerically. By solving the system of equations (4) one finds the binding energy as
TABLE I: Experimental and theoretical results for negative trion binding energies in meV for TMDCs materials. The abbreviations are the following: V- Variational Method; SVM - Stochastic Variational Method; PIMC - Path Integral Monte Carlo Method; DFT & PIMC - Density Functional Theory and Path Integral Monte Carlo Method; DMC - Diffusion Monte Carlo Method.

| TMDC  | Present work | Experiment | V [15] | SVM [18, 19] | PIMC [21] | DFT & PIMC [20] | DMC [22] |
|-------|--------------|------------|--------|-------------|-----------|----------------|---------|
| MoS₂  | 32.8         | 18±1.5     | 26     | 33.7        | 32.0      | 33.8           |         |
| MoSe₂ | 27.6         | 30 [2, 3]  | 21     | 28.2        | 27.7      | 28.4           |         |
| WS₂   | 33.1         | 10-15 [4, 30 [5], 34 [7], 45 [8] | 26     | 33.8        | 28         | 33.1           | 34.0    |
| WSe₂  | 28.3         | 30 [9, 10] | 22     | 29.5        | 28.5      | 29.5           |         |

TABLE II: Experimental and theoretical results for biexciton binding energies in meV for TMDCs materials. Notations are the same as in Table 1.

| TMDC  | Present work | Experiment | SVM [18, 19] | PIMC [21] | DFT & PIMC [20] | DMC [22] |
|-------|--------------|------------|-------------|-----------|----------------|---------|
| MoS₂  | 22.1         | 40, 60 [14], 70 [11] | 22.5     | 22.7      | 22.7           |         |
| MoSe₂ | 17.9         | ~20 [12]   | 18.4       | 19.3      | 17.7           |         |
| WS₂   | 23.1         | 45 [4, 65 [5] | 23.6     | 21        | 23.9           | 23.3    |
| WSe₂  | 19.8         | 52 [13]    | 20.2       | 20.7      | 20.0           |         |

well as the corresponding hyperradial functions. The latter allows one to construct the wave function $\Psi(\rho, \Omega_\rho)$ (3). Reasonable convergence is reached for $\mu_{max} = 10$ and we limit our considerations to this value. In calculations we use the necessary parameters for the trion and biexciton Hamiltonians that were calculated from first principles. The resulting binding energy of excitonic systems is a function of only $\rho_0$ and the electron-hole mass ratio $m_e/m_h$. In our calculations we use the effective masses extracted from the low energy band structure obtained in the density functional theory [26] or the GW approximation [27], while the screening length $\rho_0$ was calculated using the polarizibility $\chi$ for TMDCs given in Ref. [15]. The results of our calculations for the binding energy of the trion and biexciton in MoS₂, MoSe₂, WS₂, and WSe₂ along with experimental data are presented in Table 1 and Table 2. For comparison we presented the results of other theoretical studies where the Keldysh potential [23] was used to find the binding energies of trion and biexciton. Our TMDC binding energies for the trion and biexciton agree well with those calculated via the stochastic variational method using a correlated Gaussian basis [18, 19], the path integral Monte Carlo [21], diffusion Monte Carlo [22] and density functional theory and path integral Monte Carlo [20] methods. In average, the discrepancies are less than ±1 meV. However, there is significant disagreement with the variational calculations [15]. There is a discrepancy with experiment for the biexciton case for MoS₂, WS₂, and WSe₂ with all theoretical predictions, while the recent experimental result for MoSe₂ [12] is in reasonable agreement with our calculation and theoretical results [18, 22].

IV. CONCLUSION

We have applied the hyperspherical harmonics method to the calculation of binding energies for three- to four-body excitonic formations in TMDCs. Our results lie in good agreement with similar theoretical effective mass model findings for the trions and biexcitons in MoS₂, MoSe₂, WS₂, and WSe₂. There is reasonable agreement with the existing experimental binding energies for the cases of the trion in MoSe₂, WS₂, and WSe₂ and the biexciton in MoSe₂. Our disagreement with the variational calculations in the case of the trion may be due to its constraint on the symmetry of the trial wave function. However, our findings for the ground state energies for the trion and biexciton confirm and agree well with previous calculations within the aforementioned approaches where the Keldysh potential was used. The comparison of our results with existing calculations performed within different methods allows one to estimate the accuracy of the methods, and understand the importance of the screened electron-hole interaction in formation of electron-hole complexes.
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