

Time-dependent density-matrix functional theory for trion excitations: Application to monolayer MoS₂ and other transition-metal dichalcogenides

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To examine optically excited bound states, excitons and trions, in monolayer MoS₂, MoSe₂, and WSe₂, we have formulated and applied a generalized time-dependent density-matrix functional theory approach. Three different types of exchange-correlation (XC) kernels were used and their validity was evaluated through comparison with available experimental data. For excitons, we find that the local kernels, from the local density approximation and its gradient-corrected form, lead to much smaller binding energy than that extracted from experimental data, while those based on long-range (LR) interactions fare much better. The same is the case for the trion binding energy once screening effects are taken into account. Our results suggest that for both excitons and trions, the LR form of the XC kernel is necessary to describe bound states. These results confirm information from experimental data on single-layer dichalcogenides that their exciton and trion binding energies are of the order of hundreds (excitons) and tens (trions) of milli-electron volts, a result that may suggest technological application of these materials at room temperature. The proposed methodology can be straightforwardly extended to bound states with a larger number of electrons and holes than considered here.

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I. INTRODUCTION

The study of physical properties of monolayer MoS₂ is a topic of intense research these days, given the multitude of its interesting properties uncovered both experimentally and theoretically [1–16]. These efforts are part of the exploration of new types of two-dimensional (2D) materials, which potentially extend the fascinating properties of graphene. Although discovered rather recently [1], this transition-metal chalcogenide system has already recommended itself as a very promising candidate for new nanotechnological applications. In particular, contrary to the case in the bulk, monolayer MoS₂ is a direct band gap semiconductor (with an optical gap of 1.8 eV at the *K* points in the Brillouin zone) with a very high quantum efficiency for luminescence [1,2]. The system also demonstrates high electron mobility, room-temperature current on/off ratio, and ultralow standby power dissipation, with potential to be used in field-effect transistors [3]. It was shown that one can achieve complete dynamic (longer than 1 ns) valley polarization in monolayer MoS₂ by optical pumping with a circularly polarized light [4,5]. Control of the polarization in two direct band gap energy valleys (at *K* and *K'* points) could be exploited for applications in valley-based electronic and optoelectronic devices. It is thus not surprising that the optical properties of the system are of special interest and that there is a need for accurate and robust theoretical understanding of excitonic and higher order excited bound states. Experimental data suggest that excitonic effects in the system are large (binding energy ~0.2–1 eV) [1,2,6,13]. Recently, another exciting property of the MoS₂ monolayer was discovered, namely trion bound state with binding energy approximately 18 meV [7,9]. The magnitude of these binding energies suggests both excitonic and trionic effects may have applications at room temperatures. While

theoretical studies of excitons in monolayer MoS₂ have already been the subject of several studies [e.g., Refs. [8,9,12,14–16], in which the phenomenological Wannier equation and the *GW*-Bethe-Salpeter equation (*GW*-BSE) were used], those of trions are still very few. Using a trial wave function, Berkelbach *et al.* [12] were able to obtain the binding energies for both these quasiparticles, in reasonable agreement with experimental data (though ~30% overestimated for trions). It would be difficult, however, to extend their approach to the examination of excitation dynamics. Instead, time-dependent density functional theory (TDDFT) would be a better candidate (see below).

In general, an accurate description of bound states and their dynamics in semiconductors is rather messy. Excitons and trions are among the most important of these bound states. Formally, an exciton is defined as a coupled electron-hole pair, while a trion is a bound state of an exciton and an electron, so the trion can be regarded as a charged exciton (Fig. 1). While in bulk systems, the trion binding energy is typically negligible compared to that of the exciton; in constrained geometries this energy may be pronounced, leading to novel effects. The most important example is that of quantum wells, in which trion excitations affect the optical [10,11], transport [17], and diffusion properties of the system [18].

Since the standard time-dependent Hartree-Fock approximation leads to strongly overbound excitonic states, efforts have turned to the development of more subtle many-body methods, such as those based on the *GW*-BSE approach, which take into account screening and other many-particle effects correctly [19]. Unfortunately, such methodology becomes computationally very demanding for the calculation of multiple bound states (trions, biexcitons, etc.) and for strongly nonequilibrium processes (for example, ultrafast response of a system), as they require Green's functions with many time arguments. From this point of view, TDDFT [20] provides an alternative. Being a theory of one function, a space- and time-dependent electron charge density, it allows one to get an accurate numerical solution of the system response, provided that

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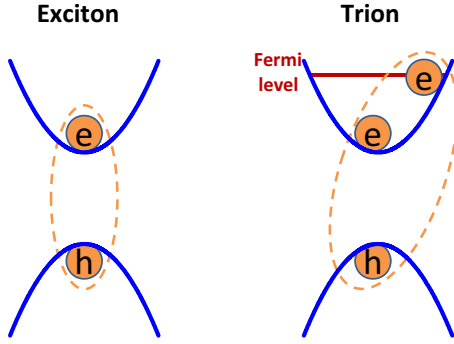


FIG. 1. (Color online) Schematic representation of the quasiparticles, exciton (left) and trion (right), in the two-band model. In the trion case, it is assumed that the exciton (electron-hole pair with energies near the band edges, i.e., with zero total momentum) is coupled to another electron at the Fermi level, the case considered in the paper.

the exchange-correlation (XC) potential describing excitonic interactions is available [21]. Some progress in incorporating such effects into TDDFT has already been made; for example, the application of a many-body Green's function [19,22,23] and the exact-exchange approximation [24,25]. However, despite good agreement with experiments, these refinements in TDDFT lead to computational complexities that are almost as demanding as the many-body formalisms. Recently, we have proposed a technically simpler and physically transparent TDDFT approach to study excitonic and biexcitonic effects [26–28]. The approach is based on the density-matrix representation of the electron wave function, and the ensuing generalized TDDFT Bloch equations allow one to calculate excitonic and biexcitonic binding energies using reasonable computational resources. In particular, the exciton equation can be regarded as the TDDFT version of the many-body exciton Wannier equation. We have demonstrated [27,28] that one can obtain rather good agreement with experimental data by choosing the proper XC kernel; for example, contact or long-range (LR) phenomenological kernels.

In this work, we generalize the density-matrix, TDDFT approach to trions and show that the formalism gives rather good agreement with experimental values for the excitonic and trion binding energies for monolayer MoS₂, as well as for two other members of the monolayer transition-metal dichalcogenide family, MoSe₂ and WSe₂, using the same XC potentials.

II. TDDFT FOR TRIONS

To derive the TDDFT equation for trion binding energy, which we define as the energy necessary to decouple one electron from the coupled electron-hole pair (exciton), we begin with a summary of the density-matrix TDDFT approach for the exciton and biexciton bound states (more details can be found in Refs. [26–28]).

(a) Excitons. In the case of excitons, one can proceed from the Kohn-Sham equation

$$i \frac{\partial \Psi_k^v(\mathbf{r}, t)}{\partial t} = H(\mathbf{r}, t) \Psi_k^v(\mathbf{r}, t), \quad (1)$$

where \mathbf{k} is the wave vector and v is the valence-band index, and the system Hamiltonian

$$H(\mathbf{r}, t) = -\frac{\nabla^2}{2m} + V_H[n](\mathbf{r}, t) + V_{XC}[n](\mathbf{r}, t) + e\mathbf{r} \cdot \mathbf{E}(t) \quad (2)$$

includes the kinetic (first), Hartree (second), and XC (third) potential terms, as well as the external homogeneous electric field (the last term). Equation (1) is solved self-consistently with the equation for the electron density, with band index l :

$$n(\mathbf{r}, t) = \sum_{l, |\mathbf{k}| < k_F} |\Psi_k^l(\mathbf{r}, t)|^2. \quad (3)$$

To solve Eqs. (1) and (2), it is convenient to use the density-matrix formalism [26], in which the wave function is expanded in terms of the basis (e.g., Bloch) static wave functions $\psi_k^l(\mathbf{r})$:

$$\Psi_k^v(\mathbf{r}, t) = \sum_l c_k^{vl}(t) \psi_k^l(\mathbf{r}). \quad (4)$$

The time-dependent coefficients $c_k^{vl}(t)$ completely describe the system dynamics. Below, we drop index v for the sake of simplicity since we will consider the case of one valence band. These coefficients can be found from the following equation:

$$i \frac{\partial c_k^m}{\partial t} = \sum_l H_{kk}^{ml} c_k^l, \quad (5)$$

where

$$H_{kq}^{lm}(t) = \int \psi_k^{l*}(\mathbf{r}) H[n](\mathbf{r}, t) \psi_q^m(\mathbf{r}) d\mathbf{r}. \quad (6)$$

However, to study the system response, it is more convenient to consider the bilinear combination of c coefficients, the density matrix:

$$\rho_{kq}^{lm}(t) = c_k^l(t) c_q^{m*}(t). \quad (7)$$

Its diagonal elements describe the level occupancies, while the nondiagonal elements describe electron transitions, including excitonic effects. The matrix elements satisfy the Liouville equation

$$i \frac{\partial \rho_{kq}^{lm}(t)}{\partial t} = [H(t), \rho(t)]_{kq}^{lm}. \quad (8)$$

In the case of two (valence v and conduction c) bands, one can derive the exciton TDDFT equation for the nondiagonal element $\rho_{kq}^{cv}(t)$ by using Eqs. (2), (3), (7) and (8). Expansion of the charge density fluctuations in Eq. (8) in terms of the density matrix elements (Eq. (6)) [by using Eq. (3)] leads to the TDDFT Wannier equation [27]:

$$[(\varepsilon_{k+q}^c - \varepsilon_k^v) \delta_{kk'} + F_{kkk'k'}^{cvvc}] \rho_{n, k'+\alpha q}^{cv}(\omega) = E_{n, q} \rho_{n, k+\alpha q}^{cv}, \quad (9)$$

where \mathbf{q} is the exciton momentum, α is the reduced hole mass, and n is the bound state number. The effective electron-hole interaction is described by the last matrix elements defined as

$$F_{kqk'q'}^{abcd}(\omega) = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_k^{a*}(\mathbf{r}_1) \psi_q^b(\mathbf{r}_1) f_{XC}(\mathbf{r}_1, \mathbf{r}_2, \omega) \psi_{k'}^{c*}(\mathbf{r}_2) \psi_{q'}^d(\mathbf{r}_2). \quad (10)$$

With $\mathbf{q} = 0$, one can obtain the excitonic binding energies from Eq. (9).

(b) Biexcitons. Similarly, one can consider the two-electron TDDFT problem in order to derive the equation for biexcitonic states [28]. In TDDFT language, this is a problem of two excited electrons in the field of two holes. The corresponding equation is

$$i \frac{\partial \Psi_{\mathbf{k}_1 \mathbf{k}_2}^{vv}(\mathbf{r}_1, \mathbf{r}_2, t)}{\partial t} = \left[H(\mathbf{r}_1, t) + H(\mathbf{r}_2, t) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \times \Psi_{\mathbf{k}_1 \mathbf{k}_2}^{vv}(\mathbf{r}_1, \mathbf{r}_2, t), \quad (11)$$

where the single-electron Hamiltonian is defined in Eq. (2), while the last term in brackets on the right-hand side describes electron-electron repulsion. The two-particle wave function can be expanded in terms of two single-electron functions:

$$\Psi_{\mathbf{k}_1 \mathbf{k}_2}^{vv}(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{l, m} B_{\mathbf{k}_1 \mathbf{k}_2}^{lm}(t) \psi_{\mathbf{k}_1}^l(\mathbf{r}_1) \psi_{\mathbf{k}_2}^m(\mathbf{r}_2), \quad (12)$$

where the two-electron matrix elements satisfy

$$i \frac{\partial B_{\mathbf{k}_1 \mathbf{k}_2}^{cd}}{\partial t} = \sum_{a, p} \left[H_{\mathbf{k}_1 p}^{ca} B_{p \mathbf{k}_2}^{ad} + H_{\mathbf{k}_2 p}^{da} B_{\mathbf{k}_1 p}^{ca} \right] + \sum_{a, b, p_1, p_2} w_{\mathbf{k}_1 \mathbf{k}_2 p_1 p_2}^{cdab} B_{p_1 p_2}^{ab}, \quad (13)$$

with $H_{\mathbf{k} p}^{ca}$ defined in Eq. (7) and

$$w_{\mathbf{k}_1 \mathbf{k}_2 p_1 p_2}^{cdab} = \frac{1}{\varepsilon_{ee}} \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{\mathbf{k}_1}^{c*}(\mathbf{r}_1) \psi_{\mathbf{k}_2}^{d*}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \times \psi_{p_1}^a(\mathbf{r}_1) \psi_{p_2}^b(\mathbf{r}_2) \quad (14)$$

is the matrix element that corresponds to electron-electron repulsion (ε_{ee} is an effective electron-electron screening parameter). Similar to the excitonic case, in order to get biexciton eigenenergies one can consider a linearized form of the corresponding Eq. (13). Indeed, if the lowest eigenenergy of this equation is smaller than the sum of two exciton energies obtained from Eq. (9), this means that two excitons form a bound state.

(c) Trions. In a similar way, one can study the case of a trion—two excited electrons described by the field $B_{\mathbf{k}_1 \mathbf{k}_2}^{ab}(t)$ in the presence of hole $c_q^{c*}(t)$. The corresponding matrix element

$$t_{\mathbf{k}_1 \mathbf{k}_2 q}^{abc}(t) = B_{\mathbf{k}_1 \mathbf{k}_2}^{ab}(t) c_q^{c*}(t) \quad (15)$$

defines the time-dependence of the three-particle wave function:

$$\Psi_{\mathbf{k}_1 \mathbf{k}_2 q}^v(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) = \sum_{l, m} t_{\mathbf{k}_1 \mathbf{k}_2 q}^{lmn}(t) \psi_{\mathbf{k}_1}^l(\mathbf{r}_1) \psi_{\mathbf{k}_2}^m(\mathbf{r}_2) \psi_q^{n*}(\mathbf{r}_3) \quad (16)$$

(the trion excitation corresponds to the upper index $lmn = ccv$). Using Eqs. (5) and (13), one can obtain the following equation for the three-particle density matrix:

$$i \frac{\partial t_{\mathbf{k}_1 \mathbf{k}_2 q}^{abc}}{\partial t} = \sum_{f, p} \left[H_{\mathbf{k}_1 p}^{af} t_{p \mathbf{k}_2 q}^{fbc} + H_{\mathbf{k}_2 p}^{bf} t_{\mathbf{k}_1 p q}^{afc} - H_{p q}^{fc} t_{\mathbf{k}_1 \mathbf{k}_2 p}^{abf} \right] + \sum_{f, m, p_1, p_2} w_{\mathbf{k}_1 \mathbf{k}_2 p_1 p_2}^{abfm} t_{p_1 p_2 q}^{fmc}, \quad (17)$$

where the H - and w -matrix elements are defined in Eqs. (6) and (14), correspondingly. Linearization of this equation gives the equation for the trion eigenenergies:

$$i \frac{\partial t_{\mathbf{k}_1 \mathbf{k}_2 q}^{ccv}}{\partial t} = (\varepsilon_{\mathbf{k}_1}^c + \varepsilon_{\mathbf{k}_2}^c - \varepsilon_q^v) t_{\mathbf{k}_1 \mathbf{k}_2 q}^{ccv} + \sum_{p_1, p_2} \left[F_{\mathbf{k}_1 q p_2 p_1}^{ccvvc} t_{p_1 \mathbf{k}_2 p_2}^{ccv} + F_{\mathbf{k}_2 q p_2 p_1}^{ccvvc} t_{\mathbf{k}_1 p_1 p_2}^{ccv} + w_{\mathbf{k}_1 \mathbf{k}_2 p_1 p_2}^{cccc} t_{p_1 p_2 q}^{ccv} \right], \quad (18)$$

where $\varepsilon_{\mathbf{k}}^c$ and $\varepsilon_{\mathbf{k}}^v$ are the free-electron and free-hole spectra, and F and w potentials describe the TDDFT electron-hole and electron-electron scattering (in particular, the first two F terms, respectively, describe the scattering of the first electron with momentum \mathbf{k}_1 on the hole with momentum \mathbf{q} , and similarly the second F term describes the scattering of the first and second electron with momenta \mathbf{k}_1 and \mathbf{k}_2 on the hole with momentum \mathbf{q}).

Equations (9), (10), (14), and (18) suggest a way of generalizing the corresponding eigenenergy equations for excitations with a larger number of bound electrons and holes than the trion. One would apply a many-particle Schrödinger equation, such as Eq. (18), in which electrons and holes attract each other with the potentials, or rather scattering matrix elements F [Eq. (10)], while the electron-electron and hole-hole repulsion potentials are defined by matrix elements w , as in Eq. (14). Thus, each pair of electrons interact through the TDDFT scattering potential:

$$w_{\mathbf{k} q; \mathbf{k}' q'}^{cccc} = \frac{1}{\varepsilon_{ee}} \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{\mathbf{k}}^{c*}(\mathbf{r}_1) \psi_{q'}^{c*}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \times \psi_{\mathbf{k}'}^c(\mathbf{r}_1) \psi_{q'}^c(\mathbf{r}_2), \quad (19)$$

which describes the scattering of two electrons with momenta \mathbf{k}, \mathbf{q} to the states with momenta \mathbf{k}', \mathbf{q}' . Similarly, one can describe the corresponding hole-hole scattering by changing all band indices from “ c ” to “ v ” in the last equation. The electron-hole attraction is described by the scattering potential

$$F_{\mathbf{k} q; \mathbf{k}' q'}^{ccvvc} = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{\mathbf{k}}^{c*}(\mathbf{r}_1) \psi_{q'}^v(\mathbf{r}_2) f_{xc}(\mathbf{r}_1, \mathbf{r}_2) \psi_{\mathbf{k}'}^c(\mathbf{r}_1) \times \psi_{q'}^{v*}(\mathbf{r}_2), \quad (20)$$

which similarly describes the scattering of the electron-hole pair from the state with momenta \mathbf{k} and \mathbf{q} to the state with momenta \mathbf{k}' and \mathbf{q}' . For example, in the case of biexciton (two electrons with momenta \mathbf{k}_1 and \mathbf{k}_2 and two holes with momenta \mathbf{q}_1 and \mathbf{q}_2), the corresponding equation for the “wave function” $B_{\mathbf{k}_1 \mathbf{k}_2 q_1 q_2}^{ccvv}$ has the following form:

$$i \frac{\partial B_{\mathbf{k}_1 \mathbf{k}_2 q_1 q_2}^{ccvv}}{\partial t} = (\varepsilon_{\mathbf{k}_1}^c + \varepsilon_{\mathbf{k}_2}^c - \varepsilon_{q_1}^v - \varepsilon_{q_2}^v) B_{\mathbf{k}_1 \mathbf{k}_2 q_1 q_2}^{ccvv} + \sum_{\mathbf{k}, \mathbf{q}} \left[F_{\mathbf{k}_1 q_1 q_2 \mathbf{k}}^{ccvvc} B_{\mathbf{k} \mathbf{k}_2 q_2}^{ccvv} + F_{\mathbf{k}_1 q_1 q_2 \mathbf{k}}^{ccvvc} B_{\mathbf{k}_1 q_2 \mathbf{k}}^{ccvv} + F_{\mathbf{k}_2 q_1 q_2 \mathbf{k}}^{ccvvc} B_{\mathbf{k}_1 \mathbf{k} q_2}^{ccvv} + F_{\mathbf{k}_2 q_1 q_2 \mathbf{k}}^{ccvvc} B_{\mathbf{k}_1 \mathbf{k} q_1}^{ccvv} \right] + \sum_{p_1, p_2} \left[w_{\mathbf{k}_1 \mathbf{k}_2 p_1 p_2}^{cccc} B_{p_1 p_2 q_1 q_2}^{ccvv} + w_{q_1 q_2 p_1 p_2}^{vvvv} B_{\mathbf{k}_1 \mathbf{k}_2 p_1 p_2}^{ccvv} \right]. \quad (21)$$

This equation has to be compared with the standard Schrödinger equation for two electrons and two holes:

$$\begin{aligned}
 i \frac{\partial \Psi_{k_1 k_2 q_1 q_2}}{\partial t} = & \left(\varepsilon_{k_1}^c + \varepsilon_{k_2}^c - \varepsilon_{q_1}^v - \varepsilon_{q_2}^v \right) \Psi_{k_1 k_2 q_1 q_2} \\
 & - \sum_k \frac{1}{k^2} \left[\Psi_{k k_2 - k q_2} + \Psi_{k k_2 q_1 - k} \right. \\
 & \left. + \Psi_{k_1 k - k q_2} + \Psi_{k_1 k q_1 - k} \right] \\
 & + \sum_{p_1, p_2} \frac{1}{k^2} \left[\Psi_{k - k q_1 q_2} + \Psi_{k_1 k_2 k - k} \right]. \quad (22)
 \end{aligned}$$

While the solution of this equation might not be less complicated than the solution of the corresponding many-body equation, the main advantage of the TDDFT approach is the inclusion of many-body effects through the two-particle attraction defined, in principle, by an exact XC kernel. This property is especially important in the strongly nonequilibrium regime with multiple excitations, in which nonlinear effects must be taken into account.

III. EXCITONS AND TRIONS IN MONOLAYER MoS₂, MoSe₂, AND WSe₂

A. The method

To calculate exciton and trion binding energies, we generate the Kohn-Sham eigenfunctions and eigenenergies using the DFT code Quantum-ESPRESSO [29] and employ the Binding Energies of Excitons (BEE) code developed in our group to obtain the necessary parameters and to solve the exciton and trion eigenenergy equations, (9) and (18). At the DFT stage, XC effects are included by applying the local density approximation (LDA) in the Perdew and Zunger parameterization [30]. In these calculations, we used norm conserving pseudopotentials [31] and a cutoff energy of 60 Ry and a $15 \times 15 \times 1$ k -point grid to represent the reciprocal space [32]. To model single layers of transition-metal dichalcogenides, as shown in Fig. 2, we used a supercell with (1×1) periodicity and ~ 15 Å of vacuum between periodic images. The calculated lattice parameter a is 3.167, 3.289, and 3.244 Å for monolayers of MoS₂, MoSe₂, and WSe₂, respectively. In the non-self-consistent calculations of the relaxed single-layer structures, we used $48 \times 48 \times 1$ k -point grid (217 independent k -points in the first Brillouin zone). The results of the band structure calculations for MoS₂ are presented in Fig. 3.

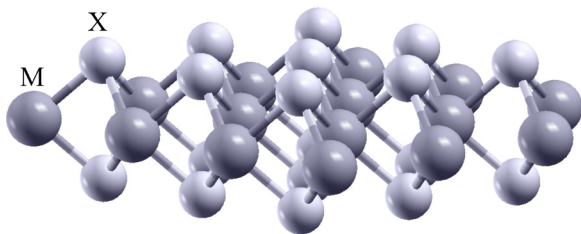


FIG. 2. (Color online) Structure of monolayer transition-metal dichalcogenides MX_2 ($M = \text{Mo}, \text{W}$; $X = \text{S}, \text{Se}$).

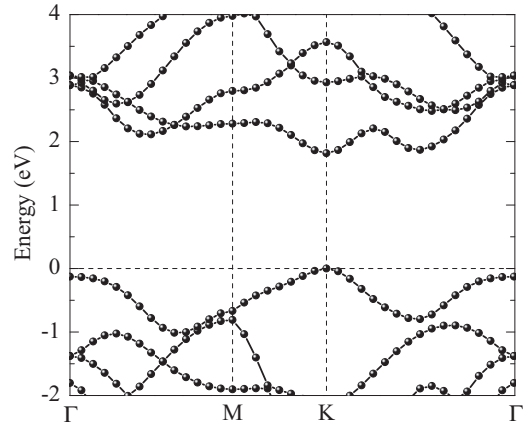


FIG. 3. Band structure of monolayer MoS₂ calculated with LDA.

Despite the standard underestimation of the band gap by LDA, our results (1.82, 1.59, and 1.72 eV for MoS₂, MoSe₂, and WSe₂, respectively) are in reasonable agreement with experimental estimations of the optical band gap [1,33]. While this agreement between the LDA and experimental results might be regarded as fortuitous, more accurate approaches that take into account screening effects, such as the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional calculations, provide results that indeed agree rather well with experimental data (HSE gives the direct gap ~ 2.2 eV [34] for MoS₂). On the other hand, the absolute value of the gap is not critical for purposes here since the binding energy is calculated with respect to the conduction band edge.

To calculate the exciton and trion binding energies, we solve Eqs. (9) and (18) using the following eight kernels (details of which can be found in Ref. [21] and references therein):

(1) Three local kernels: the first consisting of phenomenological contact interaction $f_{XC}^{\text{local}}(\mathbf{r}, \mathbf{r}') = -4\pi A \delta(\mathbf{r} - \mathbf{r}')$, where A is a parameter describing the strength of the TDDFT local electron-hole attraction, and the other two are based on LDA, with exchange (X) only and with both exchange and correlation (XC). These kernels allow us to examine how correlation, as incorporated in LDA, affects binding energies. Note that the contact kernel with $A = 1$ is the 2D LDA(X) kernel (even though MoS₂ is not exactly a 2D system, application of this kernel to it may help provide insights into how spatial constraints affect bound state energies).

(2) Three gradient-corrected kernels: one kernel with gradient-expansion approximation (GEA) and two with generalized gradient approximation (GGA; Perdew-Wang [35,36] and Perdew-Burke-Ernzerhof [PBE; [37]]). These kernels take into account the effects of possible strong spatial variation of the electronic charge; hence, the spatial dependence of the local electron-hole interaction, which may be rather important in the monolayer systems with a spatially constrained charge.

(3) Two LR kernels: phenomenological $f_{XC}(\mathbf{r}, \mathbf{r}') = -\frac{1}{\varepsilon} \frac{1}{|\mathbf{r} - \mathbf{r}'|}$, where ε is an effective screening of the electron-hole attraction, and the Slater kernel (optimized effective potential [OEP] case [38]) with physically correct electron-hole interaction, which includes a Coulomb singularity.

TABLE I. Exciton binding energy (in meV) for monolayer MoS₂ calculated with the contact kernel for different values of coupling parameter A .

A	1	0.5	0.395	0.238	0.213	0.1	Exp.
E_X	3863	1494	1000	300	200	1	220–420

B. Excitons

There is no total agreement on the values of the exciton binding energies in monolayer MoS₂, MoSe₂, and WSe₂ in the community. Thus, while the combined DFT-based phenomenological modeling approach [12] and GW -BSE [9,14–16] calculations predict extremely large binding energies for the excitons in MoS₂ (0.54 eV and 0.5–1.03 eV, correspondingly), experimental scanning tunneling microscopy/spectroscopy (STM/S) and photoluminescence (PL) analysis [13] suggest that the corresponding energy is approximately 0.22 eV (or 0.42 eV when some additional assumptions on the interpretation of the experimental data are taken into account). Similarly, in the MoSe₂ case, computational analysis [9,12] shows some difference between the calculated exciton energies and the ones obtained within the STM/STS+PL spectroscopy studies [39] (0.47 eV and 0.91 eV vs 0.55 eV). Berkelbach *et al.* [12] and Ramasubramaniam [9] also performed calculations of the exciton energy for WSe₂ to obtain exciton binding energy of 0.45 eV and 0.9 eV, respectively, which again overestimate the spectroscopically measured value of 0.37 eV [40]. The results for the binding energy of excitons for the systems of interest, calculated with the above kernels, are presented in Tables I–III and Figs. 4 and 5. In the case of MoS₂, we find that the contact kernel can reproduce experimentally estimated energy 0.3 eV [13] at $A = 0.238$. We also find that the exciton binding energy is very sensitive to the value of A (Table I and Fig. 4). To test the ability of the contact kernel to describe excitons in other transition-metal dichalcogenides, we extended our calculations to single-layer MoSe₂ and WSe₂. As shown in Fig. 4, the values of A for the three different dichalcogenides are very similar (~ 0.2 – 0.4). Taking into account the oversimplification in the contact approximation, this result is quite remarkable.

On one hand, LDA with either X or XC gives very small binding energies (~ 1 – 10 meV, Table II). Comparing this result to that obtained for the contact kernel, and taking into account the fact that A is of order 1 (2D LDA), one can suggest that indeed the spatial constraint in one direction may be important for excitons in these system. On the other hand, a very small decrease of the LDA binding energy with inclusion of the correlations suggests that they are not very important in these materials (though the situation may change dramatically when

TABLE III. Exciton binding energy for MoS₂ (in meV) for the LR kernel and different values of ε .

ε	0.449	0.752	0.844	1	2.8	4.2	3.3	Exp.
E_X	1000.00	300	200	90.54	0.62	0.39	0.51	220–420 [13]

one dopes the system with transition-metal atoms). We also found that charge-gradient correction does not improve the situation significantly. The GEA and PW91 binding energies are even lower than LDA ones. Though PBE gives much larger energies than LDA, it is still much lower than the experimental values. It is also worthwhile to note that the LDA and GGA exciton energies for MoSe₂ are an order of magnitude larger than that for other two materials, which display very similar values. The d states of the Se atoms with more localized charge densities may be playing a role here.

The results for the exciton binding energy change dramatically when one takes into account the Coulomb nature of the interaction (a kernel with $\frac{1}{q^2}$ singularity [see, e.g., Refs. [24]–[26]]). While the unscreened ($\varepsilon = 1$) phenomenological LR kernel gives underestimated values of the binding energy (Table III, Fig. 5), the Slater kernel results are in reasonable agreement with the experiment [13,39,40] and other calculations [9,12,14–16] (Table II). In the LR case, the results are very sensitive to the value of the screening parameter ε , and one can obtain the experimental energy by lowering the screening parameter by $\sim 20\%$ to the vacuum (unscreened) value. Interestingly, similar to the local case, the value of the fitting (screening) parameter has the same order of magnitude in all three cases (Fig. 5). On the other hand, it seems problematic to get accurate experimental binding energy if one uses experimentally motivated values of the screening parameter. In particular, in the case of MoS₂, the parallel and perpendicular components of the dielectric constant are $\varepsilon_{\parallel} = 2.8$ and $\varepsilon_{\perp} = 4.2$ [8], and their average is $\bar{\varepsilon} = \sqrt{(2\varepsilon_{\parallel}^2 + \varepsilon_{\perp}^2)}/3 \approx 3.3$, which corresponds also to the dielectric constant of bulk MoS₂ [41]. E_X is extremely sensitive to the value of screening at $0.5 < \varepsilon < 3$ – 4 (Table III, Fig. 5). It suggests that this potential will result in an accurate description of exciton effects when used as a part of a hybrid potential, for example with one of GGAs.

It must be emphasized that in our calculations we do not include spin-orbital band splitting whose inclusion would have resulted in two exciton peaks (the band splitting is much smaller than the exciton and trion excitation energies). The inclusion of spin-orbit effects is, however, straightforward. Namely, in this case one needs to consider two split valence bands, which will transform the exciton and trion Eqs. (9)

TABLE II. Exciton binding energy (in meV) calculated with seven remaining kernels for the three materials. In the case of LDA, both X and XC results are presented, while in the GEA, PW91, and PBE cases, only the X result is shown. For LR, we use the screening parameter $\varepsilon = 1$.

	LDA (X)	LDA (XC)	GEA	PW91	PBE	LR	Slater	Exp.
MoS ₂	2.05	2.00	0.87	1.96	10.46	90.54	1093	220–420 [13]
MoSe ₂	14.81	14.45	1.21	12.58	39.34	187	1183	550 [39]
WSe ₂	1.20	1.19	0.53	1.63	2.25	9.81	734	370 [40]

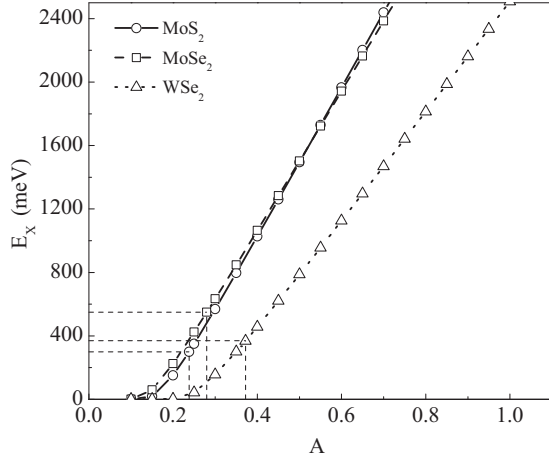


FIG. 4. Exciton binding energy (in meV) calculated with the contact kernel for different values of coupling parameter A for monolayer MoS_2 , MoSe_2 , and WSe_2 . The dashed lines mark the experimental values for E_x (see Refs. [13,39,40]) and the corresponding A s.

and (18) into 2×2 matrix equations (in the band indices). The band splitting will lead to two exciton peaks separated by approximately the band-splitting energy.

C. Trions

Equation (18) for the trion energy is rather complicated to be solved exactly; therefore, we use an approximation similar to that used in the many-body approach. Namely, it is convenient to reduce the problem to that of an electron with momentum \mathbf{k}_1 in the presence of an exciton comprised of the remaining electron and hole (momenta \mathbf{k}_2 and \mathbf{q}). In this case, using Eq. (9) for the exciton function, one can transform Eq. (18) to

$$i \frac{\partial t_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{q}}^{ccv}}{\partial t} = \left(\varepsilon_{\mathbf{k}_1}^c + E_{X \mathbf{k}_2, \mathbf{q}} \right) t_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{q}}^{ccv} + \sum_{\mathbf{p}_1, \mathbf{p}_2} \left[F_{\mathbf{k}_1 \mathbf{q} \mathbf{p}_2 \mathbf{p}_1}^{cvvc} t_{\mathbf{p}_1 \mathbf{k}_2 \mathbf{p}_2}^{ccv} + w_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{p}_1 \mathbf{p}_2}^{cccc} t_{\mathbf{p}_1 \mathbf{p}_2 \mathbf{q}}^{ccv} \right]. \quad (23)$$

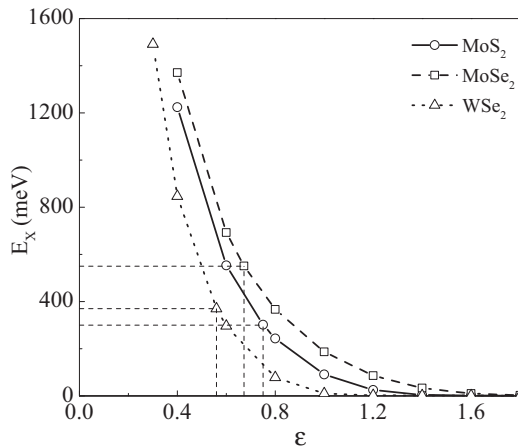


FIG. 5. Exciton binding energy (in meV) for the LR kernel and different values of ε for the three materials. The corresponding experimental values [Refs. [13,39,40]] are marked by dashed lines.

Next, we assume that the excitonic electron and hole momenta are fixed, $\mathbf{k}_2 = \mathbf{q}$, i.e., we consider the exciton with fixed center-of-mass. The trion equation now reduces to

$$i \frac{\partial t_{\mathbf{k}_1 \mathbf{q} \mathbf{q}}^{ccv}}{\partial t} = \left(\varepsilon_{\mathbf{k}_1}^c + E_{X \mathbf{q}, \mathbf{q}} \right) t_{\mathbf{k}_1 \mathbf{q} \mathbf{q}}^{ccv} + \sum_{\mathbf{p}_1, \mathbf{p}_2} \left[F_{\mathbf{k}_1 \mathbf{q} \mathbf{q} \mathbf{p}_1}^{cvvc} t_{\mathbf{p}_1 \mathbf{q} \mathbf{q}}^{ccv} + w_{\mathbf{k}_1 \mathbf{q} \mathbf{p}_1 \mathbf{q}}^{cccc} t_{\mathbf{p}_1 \mathbf{q} \mathbf{q}}^{ccv} \right] = 0, \quad (24)$$

which is equivalent to the following eigenenergy equation:

$$\left(\varepsilon_{\mathbf{k}}^c + E_{X \mathbf{q}, \mathbf{q}} - \omega \right) \delta_{\mathbf{k} \mathbf{p}} + F_{\mathbf{k} \mathbf{q} \mathbf{q} \mathbf{p}}^{cvvc} + w_{\mathbf{k} \mathbf{q} \mathbf{p} \mathbf{q}}^{cccc} = 0. \quad (25)$$

We assume that the exciton is created in one of two equivalent \mathbf{K} -points, which correspond to the direct band gap transition, and put \mathbf{q} equal to the \mathbf{K} -point momentum. While it is easy to generalize the solution to arbitrary exciton momenta, the trion energy obtained with this approximation is sufficient to estimate the energy scale of the trionic effects in the system, including the position of the trion peak in the optical absorption spectrum.

Before presenting our results for the trion binding energy, we summarize the experimental data known to us for the three systems. Absorption and PL (MoS_2) [7], differential reflectance and PL (MoSe_2) [42], and PL (WSe_2) [43] measurements give ~ 18 meV (MoS_2) and ~ 30 meV (MoSe_2 and WSe_2) as the trion binding energies. The results of the solution of Eq. (25) using the contact kernel with $A = 0.238$ (the case of characteristic exciton energy 0.3 eV) at different values of the electron-electron screening for MoS_2 are summarized in Fig. 6. Clearly, the results are very sensitive to the value of ε , though one can successfully reproduce the experimental result 18 meV [7] at a reasonable value $\varepsilon \sim 11$. We did not find a finite binding energy when using the LDA, GEA, and GGA kernels, a naturally expected result because of the extremely low excitonic energies obtained from these kernels (see Table II, in which all the results for the local kernels are summarized). The results in Tables I and II suggest that while the TDDFT

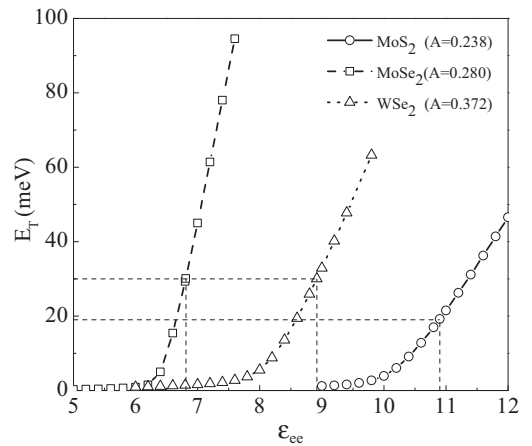


FIG. 6. The trion binding energy (in meV) obtained with the contact kernel (with A corresponding to exciton energy of 300, 550, and 370 meV for MoS_2 , MoSe_2 , and WSe_2 , respectively) at different values of the electron-electron screening parameter ε_{ee} . Again, the corresponding experimental values are marked by dashed lines.

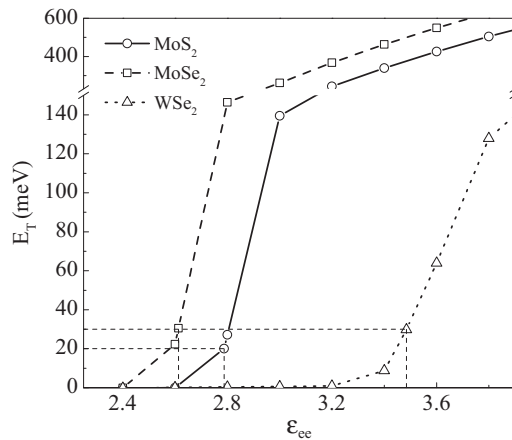


FIG. 7. The trion binding energy (in meV) obtained with the Slater kernel and different values of the electron-electron screening parameter for the three materials. The dashed lines correspond to experimental values [12].

exciton energies can be obtained by assuming even a local electron-hole attraction, to get a bound state of an electron and an exciton, one needs to take into account the LR character of the interaction (LR interaction also reproduces correct exciton energies). Indeed, the electron-exciton interaction is more of “a dipole” type, contrary to the Coulomb interaction of the electron and hole. As for excitons, the fact that the contact kernel (2D LDA) results in a finite trion binding energy, contrary to that for the bulk with LDA, suggests that the spatial constraint (charge nonhomogeneity) of the system is important in this case too. We find very similar results for the trion energy for the other two single-layer dichalcogenides by using the local attraction and screened Coulomb repulsion (Fig. 6). In particular, the value of the screening parameter necessary to reproduce correct trion energy has the same order of magnitude for all three materials.

In the case of LR kernels, we find that the trion energy is sensitive to the value of the electron-electron screening. In particular, for MoS₂ one can easily reproduce the experimental binding energy with the Slater kernel at fair value $\epsilon \sim 2.7$. Similar results were found for the other two materials, with the close values for the fitting screening parameter (Fig. 7).

IV. CONCLUSIONS

In this paper, we have formulated a density-matrix TDDFT approach to examine the energies of trions in bulk systems, as well as in nanomaterials. This approach is physically transparent, with the interparticle interaction defined by the TDDFT XC kernel. Similar to the formalism for excitons, this methodology has several advantages over standard many-body approaches: simplicity and accurate accounting of many-body correlation (especially screening) effects.

We applied the approach to study exciton and trion binding energies in monolayer MoS₂, MoSe₂, and WSe₂. There are experimental indications that the corresponding binding energies in these materials are rather large (~ 0.2 – 0.5 eV [13,39,40] and 0.02 – 0.03 eV [7,42,43]), which makes it possible to use the exciton and trion effects at room temperatures. We show a theoretical confirmation of these high binding energies when we employ a LR Slater XC kernel, which takes into account correctly the nature of the electron-hole interaction. We find some phenomenological kernels (one LR and one contact) with physically reasonable values of parameters to also provide reasonable binding energies. On the other hand, we find that for both excitons and trions, one cannot obtain finite (non-negligible) values with standard LDA and GGA kernels as a result of the missing LR nature of the electron-hole interaction. The reasonable agreement with experimental values for three different monolayer transition-metal dichalcogenides suggests the universality of the proposed potentials.

The formalism described above can be used to study binding energies and ultrafast processes that involve excitonic, trionic, and biexcitonic effects. The scheme proposed in the paper can be easily generalized to bound states with larger number of quasiparticles.

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