Screening effect for excitonic spectrum of Coulomb coupling between two Dirac particles.

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Abstract. The properties of screening effect for energy spectrum of excitons in monolayer transition metal dichalcogenides are investigated using a multiband model. The excitonic Hamiltonian in the product base of the Dirac single-particle is used. The corresponding energy eigenvalue system of the first order ODE (radial equations) was solved using the finite difference method. This enables to determine the energy eigenvalues of the discrete excitonic spectrum and the wave functions. We compare the results for the energy spectrum and the corresponding eigen-functions forms for WS\textsubscript{2} and WSe\textsubscript{2} computed for two different potentials: pure Coulomb and screened Coulomb (Keldysh potential). It is demonstrated that excitonic energy levels for unscreened potential lie deeper, and the corresponding eigen-functions’ forms differ from those obtained for screened one.

1. Introduction
In this paper, the properties of excitonic energy spectrum in transition metal dichalcogenide (TMD) monolayers are investigated using a multiband model. The starting point of our analysis is the excitonic matrix Hamiltonian in the product base of Dirac single-particle states constructed in [1]. Such Hamiltonian accounts for spin-orbit coupling. Following the separation of variables with respect to polar coordinates, we decouple the corresponding matrix eigenvalue problem rigorously and solve the resulting second order ODE by means of finite difference method (FDM). It is worth remarking that similar reduction for the matrix Hamiltonian energy eigenvalue problem was performed in papers [2], [3], [1], [4]. However, in these papers the reduction was approximate. In our approach the reduction to the second order resulting ODE for radial wave function is exact.

We determine excitonic energy levels and corresponding wave functions. Analysis the resulting radial ODE in both case when Coulomb or Keldysh potential is applied, we demonstrate that the discrete excitonic spectrum lies exactly below the value of the energy gap. In this paper we present a comparison analysis of the results for the energy spectrum and the corresponding eigen-functions for WS\textsubscript{2} and WSe\textsubscript{2}. These were computed by means of FDM for case of two different potentials: pure Coulomb and screened Coulomb (Keldysh potential). We demonstrate that Coulomb potential levels of excitonic energy spectrum are located lower compare to eigen-levels for the Hamiltonian with Keldysh interaction potential.

According to [1], the exciton Hamiltonian is constructed in the basis \( \langle \phi^\text{C}_\text{e} \otimes \phi^\text{C}_\text{c} \rangle, \langle \phi^\text{C}_\text{e} \otimes \phi^\text{C}_\text{v} \rangle, \langle \phi^\text{C}_\text{v} \otimes \phi^\text{C}_\text{c} \rangle, \langle \phi^\text{C}_\text{v} \otimes \phi^\text{C}_\text{v} \rangle \rangle^T \), i.e. the basis spanning the total Hilbert space that is given by the set of all possible tensor products combinations for the atomic orbital states of individual
particles at the conduction and valence band edges. Using the orthonormality of the basis functions, the total exciton Hamiltonian (the symbol of the operator) could be written in the form introduced in [1] (see formulae (4) and (5)) with the Keldysh potential \(-V(r)\) in polar coordinates that is given by

\[
V(r) = V_0 \frac{\pi}{2} \left( H_0 \left( \frac{r}{r_0} \right) - Y_0 \left( \frac{r}{r_0} \right) \right), \quad V_0 = \frac{e^2}{4\pi\varepsilon_0\chi r_0^2 t}, \quad \chi = \varepsilon_1 + \varepsilon_2,
\]

where \(Y_0(r)\) and \(H_0(r)\) are Newmann and Struve functions, respectively, \(r_0\) is the screening length (the characteristic space scale of the problem), \(t_h\) is the hopping parameter, \(\varepsilon_{1,2}\) is the dielectric constant of the environment above and below the TMD monolayer. It is worth noting that \(at_h = v_F t_h\), where \(v_F\) is the Fermi velocity and \(a\) is the lattice constant. For the case of Coulomb potential we have \(V(r) = V_0/(r/r_0)^2\).

The eigenvalue problem for this Hamiltonian \(H^{exc}_\alpha(k^e, k^h, r_{eh})|\Psi_{\alpha,n}\rangle = E^{exc}_\alpha(k^e, k^h)\langle\Psi_{\alpha,n}|\) defines the exciton energy \(E^{exc}_\alpha(k^e, k^h, r_{eh})\) and the exciton eigenstate \(|\Psi_{\alpha,n}\rangle\), where \(\alpha\) is a notation for the set of the spin and the valley indices \(s_e, \tau_e, s_h, \tau_h\) with the values \(\pm 1\) for the electron-hole Dirac particles, \(k^e, k^h\) are wave vectors, \(n\) means a set of quantum numbers of the excitonic states of discrete spectrum ([1]). The above eigenvalue problem is a matrix equation which, following a procedure analogous to [1] and [3], can be decoupled to a single ODE of the second order.

2. Excitonic Hamiltonian and separation of variables.

Let us consider the excitons with zero center-of-mass momentum \(K = k_e + k_h = 0\). Introducing \(k = k_e = -k_h\) and using transformation to dimensionless polar coordinates \(\partial_x = \cos \varphi \partial_r - \frac{\sin \varphi}{r} \partial_\varphi\), \(\partial_y = \sin \varphi \partial_r + \frac{\cos \varphi}{r} \partial_\varphi\), we can write exciton Hamiltonian (see Ref. [1]) in the following way:

\[
\begin{pmatrix}
-V(r) & -he^{i\tau_h\varphi}D_h^- & -he^{-i\tau_e\varphi}D_e^+ & 0 \\
-he^{i\tau_h\varphi}D_h^+ & \Delta_h - V(r) & 0 & -he^{-i\tau_e\varphi}D_e^+
\end{pmatrix}.
\]

We define here differential operators \(D_{\pm} = i\tau_{x,y} \partial_{x,y} \pm \partial_{\varphi}/r\) and quantities \(\Delta_{\pm,\tau} \equiv \Delta - \lambda s_{s,\tau} t_{e,h}\) (the effective band-gap, see [1]) with \(\lambda\) being the spin-orbit coupling strength. \(\Lambda \equiv \lambda (s_e \tau_e - s_h \tau_h)\), and \(h = a/r_0 = v_F t_h/(r_0 t_h)\) is the dimensionless parameter. We have also expressed energy quantities \((\Delta, \lambda, V(r) etc.)\) in the hopping parameter \(t\) units and the spatial variables in the screening length \(r_0\) ones.

Due to spin splitting of the valence band, there are effectively two band gaps and, as a consequence, two different types of excitons (see [1]). These are commonly referred to as A and B excitons. The method presented in this paper can be applied with both values of \(s_h \tau_h = \pm 1\). When \(s_h \tau_h = 1\) the Hamiltonian (2) describes the A exciton, while \(s_h \tau_h = -1\) relates to the B exciton. The A excitons in the \(K\) and \(K'\) valley have \(s_e = 1, \tau_e = 1, s_h = -1, \tau_h = -1\) and \(s_e = -1, \tau_e = -1, s_h = 1, \tau_h = 1\), respectively. The B exciton has \(s_e = -1, \tau_e = 1, s_h = 1, \tau_h = -1\). Hence, we obtain \(\Lambda = 0\). For the A exciton in the \(K\) and \(K'\) valley (see [1]) we get \(\Delta_h = \Delta_e = \Delta - \lambda = \Delta_{s,e}\). For the B exciton in the \(K\) valley (see [1]) we get \(\Delta_h = \Delta_e = \Delta + \lambda\). Therefore, we can express \(\Delta_h\) and \(\Delta_e\) in terms of \(\Delta_{s,\tau}\).

In order to separate variables for the \(A\) and \(B\) excitons in the \(K\) valley, we use the ansatz

\[
\psi(r, \varphi) = e^{i\varphi} \begin{pmatrix} \psi^{(1)}_e(r) e^{-i\varphi}, \psi^{(2)}_e(r), \psi^{(3)}_e(r), \psi^{(4)}_e(r) e^{i\varphi} \end{pmatrix}^T,
\]
where \( l \in \mathbb{Z} \) is an orbital quantum number. Thus, the Hamiltonian (2) acting on \( \psi_l(r) = \left( \psi_l^{(1)}(r), \psi_l^{(2)}(r), \psi_l^{(3)}(r), \psi_l^{(4)}(r) \right)^T \) takes the form \( \hat{H}_l \psi_{nl}(r) = E_{nl} \psi_{nl}(r), n = 0, 1, 2, ..., \) with the radial quantum number \( n \), and can be represented as the following system of four first-order ODE:

\[
\begin{align*}
V_E \psi_l^{(1)}(r) + hi \left( \partial_r + \frac{l}{r} \right) \psi_l^{(2)}(r) - hi \left( \partial_r + \frac{l}{r} \right) \psi_l^{(3)}(r) &= 0, \\
\left( \partial_r - \frac{l+1}{r} \right) \psi_l^{(1)}(r) - ih^{-1}(\Delta_{s,\tau} + V_E) \psi_l^{(2)}(r) - \left( \partial_r + \frac{l}{r} \right) \psi_l^{(4)}(r) &= 0, \\
\left( \partial_r - \frac{l-1}{r} \right) \psi_l^{(2)}(r) + ih \left( \partial_r - \frac{l+1}{r} \right) \psi_l^{(3)}(r) + V_E \psi_l^{(4)}(r) &= 0,
\end{align*}
\]

(3)

where \( V_E = -V(r) - E \). Transforming vector components \( \psi_l(r) \) into \( \phi_l^{(1,4)} = \psi_l^{(1)}(r) \pm \psi_l^{(4)}(r) = \psi_l^{(2)}(r) \pm \psi_l^{(3)}(r) \), we obtain a new system of ODE for the components of a new vector \( \phi_l(r) = \left( \phi_l^{(1)}, \phi_l^{(2)}, \phi_l^{(3)}, \phi_l^{(4)} \right)^T \). This system is reduced into a scalar second-order ODE:

\[
\left( \frac{\phi_l^{(3)}}{r} \right)'' + \left( \frac{l}{r} - \frac{V'}{V_E} \right) \left( \frac{\phi_l^{(3)}}{r} \right)' + \left( \frac{V_E^2 - \Delta_{s,\tau}^2}{4\hbar^2} - \frac{l^2}{r^2} \right) \phi_l^{(3)}(r) = 0.
\]

(4)

As soon as we solved spectral problem (4) for \( 0 < E < \Delta_{s,\tau} \) and found \( \phi_l^{(3)}(r) \), one could evaluate other components of \( \phi_l(r) \) and, finally, the components \( \psi_l(r) \).

3. Screening effect for \( A \) exciton in \( K \) valley - numerical analysis

We consider the special case \( s_h = \tau_e = 1, s_b = \tau_h = -1 \) which corresponds to \( A \) exciton in \( K \) valley (see [1]). We solve our spectral problem for (4) using FDM. We take into account that the eigenfunction must decay exponentially. Fig. 1 shows comparison between the excitonic spectra \( E_{nl} \) for the s- and p-states \( (l = 0, 1) \) with \( n = 0, 1, 2, 3 \) obtained for Keldysh and Coulomb potentials in WS\(_2\) with the parameters \( \Delta_{s,\tau} = 2.4 \) eV, \( r_0 = 3.789 \) nm, \( a = 0.3197 \) nm, \( t_h = 1.25 \) eV, and WSe\(_2\) with \( \Delta_{s,\tau} = 1.97 \) eV, \( r_0 = 4.511 \) nm, \( a = 0.3317 \) nm, and \( t_h = 1.13 \) eV. Both examples involve the SiO\(_2\) substrate with \( \varepsilon = 3.9 \). In Fig. 2, the probability distributions data for the case \( n = 0 \) and \( l = 0 \) are shown for Keldysh potential - (a) and for the Coulomb potential - (b), presenting \( |\psi_{00}^{(1,2,3)}|^2 \) dependence on \( r \) for WS\(_2\).
Figure 2. The probability distributions data for the case \( n = 0 \) and \( l = 0 \), shown in (a) for Keldysh and in (b) for Coulomb potentials, presenting \( |\psi_{(1,2,3)}^{00}|^2 \) dependence on \( r \) for WS\(_2\).

We would like to remark that the binding energy \( E_b = \Delta_{s,T} - E_{00} \), computed from experimental data for WS\(_2\) and WSe\(_2\) (see [5], [6]) is more efficiently described by Coulomb potential. Namely, we have \( E_b = 0.29 \) eV (see [5]), and the values for Coulomb and Keldysh potentials are \( E_b = 0.272 \) eV and \( E_b = 0.18 \) eV, respectively. Regarding the experimental data for WSe\(_2\) we obtain \( E_b = 0.31 \) eV (see [6]), and the values for Coulomb and Keldysh potentials are \( E_b = 0.259 \) eV and \( E_b = 0.16 \) eV, respectively. Thus, one could see that the Coulomb potential model is more realistic for the discussed examples.

4. Conclusion
The energy spectrum of excitons in monolayer TMD has been calculated using a multiband model. Following the separation of variables, we decoupled the corresponding system of the first order ODE for the radial eigen-vector components rigorously and solved the resulting second order ODE by means of FDM. We compared the results for the energy spectrum and the corresponding eigen-functions for WS\(_2\) and WSe\(_2\) computed for two different potentials: Coulomb and Keldysh. It was shown that the Coulomb levels of excitonic energy spectrum are located lower, and the corresponding eigen-functions look differently. The energy levels perturbation appears stronger for the lowest states. The screening contributes most to the ground state shift.

5. Acknowledgments
The authors would like to thank Dr. A. Vagov, Dr. D. Gulevich for helpful discussions. This work is supported by the Russian Science Foundation under the grant 18-12-00429.

6. References
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