Solving Schrodinger Equation for Excitons in Multilayered Media

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***Abstract*—For the modeling of electron-hole interactions occurring in atomically thin transition metal dichalcogenides, the Keldysh approximation has been used in the recent literature. This work first explains how the exact Coulomb interaction energy can be evaluated for electron-hole pairs in a general multilayered medium and compares approximate and exact potentials. Then the influence of using approximate or exact Coulomb potential in a Schrodinger equation solver is discussed.**

I. Introduction

Atomically thin layered transition metal dichalcogenides (TMDs) have received a growing attention in the past decade due to their remarkable physical properties [1]–[8]. Even though bulk and thin TMD films are well known materials [9], it took almost 40 years to precisely obtain them in the monolayer form. Recent studies have proven that the excitonic properties of atomically thin TMDs differ from their bulk state. In contrast to bulk, the electron and hole forming an exciton in monolayer TMDs are strongly confined to the plane of the monolayer. Hence monolayer TMDs, which are direct-gap semiconductors with bandgaps in the visible regime, exhibit strong sub-bandgap photoexcitations at room temperature owing to weak dielectric screening and binding energies of at least several hundred meVs.

Spectroscopy experiments conducted on TMD coated substrates have shown that both original spectrum and its derivative have minima (or maxima depending on the experiment type) at certain wavelengths. The dips observed in the reflectance spectra are considered as a natural outcome of excitonic resonance and wherever they occur are named as exciton A, B, C, $\cdots$ transition energies [1], [2], [9]. The dips observed in the derivative of the reflectance spectrum are referred as 1s, 2s, 3s, $\cdots$ states of these excitons [1], [2].

The behavior of these states are different than the usual hydrogenic Rydberg series of energy levels of the excitonic states. The main mechanism behind this non-hydrogenic exciton behavior is explained by "anti-screening", where the effective screening is reduced due to the fact that a larger portion of the electric field is located in the surrounding low-dielectric medium as the spatial separation between the electron and hole increases. In order to quantify this observation, an approximate formula for the Coulomb interaction energy is used in [1] within a 2D effective mass Hamiltonian. This approximation was originally developed by Keldysh [10] and yields results which are close to experimental results when the screening length and the band gap energy are taken as free parameters. However, the researchers use a very large screening length than what Keldysh formula suggests to get a better agreement with experiment results.

The first aim of this work is to remove the ambiguity of screening length value by calculating the Coulomb interaction via Sommerfeld integration rather than the Keldsyh formula. The second aim is to determine when it is safe to use the Keldysh approximation. Third aim is compare Schrodinger equation solvers implemented with approximate and exact Coulomb potentials to calculate exciton transition energies of monolayer TMDs.

II. Theory

Figure 1 shows a multilayered medium with N-layers, where layer-i exists between z_{i-1} and z_i and characterized with its permittivity ϵ_i for $i = 1, 2, \cdots, N$. $z_0 = -\infty$ and $z_N = \infty$. q_s and q_t are the two charges in layer-m and layer-n and located at (x_s, y_s, z_s) and (x_t, y_t, z_t), respectively.

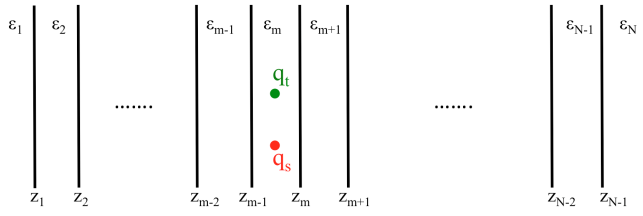

Fig. 1. Schematic illustration of two charges (q_s and q_t) in a multilayered medium with N-layers.

The Coulomb interaction energy between these two charges can be calculated by evaluating the Sommerfeld integral

$$V = q_s q_t \int_0^\infty \int_0^\infty \Big\{ \frac{2\delta_{st}}{\epsilon_m \pi \gamma} e^{-\gamma|z_t - z_s|} + A_n e^{\gamma z_t} + B_n e^{-\gamma z_t} \Big\} \cos(\alpha \Delta x) \cos(\beta \Delta y) d\alpha d\beta, \quad (1)$$

where $\Delta x = x_t - x_s$, $\Delta y = y_t - y_s$ $\gamma = \sqrt{\alpha^2 + \beta^2}$ and δ_{mn} is the delta function (i.e. $\delta_{mn} = 1$ if $m = n$, otherwise it is zero). The coefficients A_i's and B_is can be found by enforcing the boundary conditions on the interfaces: $V^2(z_i^-) = V^2(z_i^+)$

and $\epsilon_{i-1}\partial V^2(z_i^-)/\partial z = \epsilon_i \partial V^2(z_i^+)/\partial z$. Even though we are interested in excitons confined in the TMD layer, Eq. (1) is valid for any electron-hole pair.

Almost a half century ago, Keldysh studied the Coulomb interaction energy of electron-hole pairs for thin films [10] and developed the approximate formula

$$V_{approx} = \frac{\pi q_s q_t}{\epsilon_2 d}\left[H_0^{(2)}\left(\frac{\rho}{\rho_0}\right) - N_0^{(2)}\left(\frac{\rho}{\rho_0}\right)\right] \qquad (2)$$

for the evaluation of this interaction energy between two charges separated with a distance ρ existing in a high index thin film surrounded by low index media. Note that in Eq.(2), he deals with a 3 layer media, where the second layer is the semiconductor. So that $d = z_2 - z_1$, $\rho_0 = d\epsilon_2/(\epsilon_1 + \epsilon_3)$, $H_0^{(2)}$ and $N_0^{(2)}$ are zeroth order Bessel and Struve functions of second kind. It should be also noted that this formula provides a good approximation only if $\epsilon_{1,3} \ll \epsilon_2$ and $d \ll \rho$, where a_0 is the exciton radius.

For the numerical solution of Schrodinger equation $\hat{H}\psi_n = E\psi_n$ with the finite differences method, we employ the following Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_\rho^2 - V(\rho) \qquad (3)$$

with the effective mass approximation, where the effective mass is given by $\mu^{-1} = m_e^{-1} + m_h^{-1}$, m_e and m_h are the mass of an electron and a hole, respectively.

III. Numerical Results

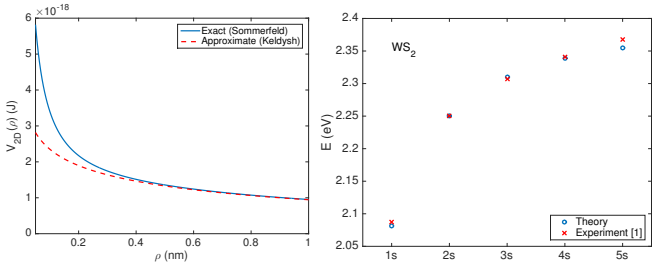

Fig. 2. *Left:* Coulomb interaction energy calculated with Sommerfeld integration (blue solid line) and approximate formula (red dashed line) for a 3-layer media with dielectric permittivities of 2.25, 12, and 1. *Right:* Numerically obtained transition energies (blue circles) for the excitonic states are compared to experimental results (red circles) [1] for monolayer WS_2 placed on top of SiO_2/Si substrate.

To determine the accuracy limits of the Keldysh approximation, we calculate the Coulomb energy of two unitary charges in the middle of a 0.7 nm thick dielectric film with a permittivity of 12, where the bottom and top layers permittivities are 2.25 and 1, respectively, using Eqs. (1) and (2). As shown in the left half of Fig. 2, indeed Sommerfeld integration and Keldysh formula lead to almost same energies when ρ is 0.7 nm or bigger but at short distances, the difference is non-negligible. From the physical point of view, the approximate formula can definitely help us to understand and visualize dielectric screening of excitons at long range. However, this formula should be used for the numerical solution of the Schrodinger equation due to its inaccuracy at short ranges.

In the second part, we utilize the approximate and exact Coulomb potentials in our finite-difference Schrodinger equation solver. We assume there is a 0.7 nm thick TMD layer on top of SiO_2/Si substrate. Relative permittivities of SiO_2 and Si are taken as 2.2 and 15 respectively, which refer to their average permittivities in the visible range of the electromagnetic spectrum. The thickness of the oxide layer is 300 nm. The reduced effective mass is assumed to be $0.25m_e$ [4], [5]. Interestingly, when we use a permittivity of 3.9 for TMD (which is the out of plane permittivity of WS_2), our Schrodinger equation solver utilized with the exact potential gives exciton A, B, and C transition energies; and when we use a permittivity of 12 for TMD (which is the in plane permittivity of WS_2), our Schrodinger equation solver gives 1s, 2s, 3s, $\cdots$ transition energies for the exciton A [1], as shown in the right side of Fig. 2. However, the Schrodinger equation solver utilized with the approximate Coulomb potential does not produce realistic results, which will be discussed at the conference.

IV. Conclusions

Keldysh approximation can be used to calculate the interaction energy of electron-hole pairs that are not very close to each other but it should not be utilized in Schrodinger equation solvers to analyze TMD excitons. For this purpose, the exact Coulomb potential should be evaluated via Sommerfeld integration. Further research is needed in order to take anisotropic nature of TMDs into account.

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