Mirror particle effects in kinetic Monte Carlo simulations including Coulomb interaction with periodic boundaries

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***Abstract*—We investigate the photoluminescence of low-dimensional disordered materials, as used e.g. in solar cells, by performing kinetic Monte-Carlo simulations of exciton hopping with periodic boundary conditions. In order to perform numerically efficient calculations, the box length L_{box} should be as small as possible while maintaining physically meaningful results during the presence of exciton-exciton-interaction. Exciton-exciton interaction can be approximated by attractive dipole-dipole-interaction in the limit of long distances. We study the convergence of a direct summation approach instead of the Ewald summation technique.**

***Index Terms*—Monte Carlo simulation, photoluminescence, excitons, low-dimensional semiconductors, periodic boundaries**

I. Introduction

Complex physical systems comprising a large number of particles and interactions are often inaccessible to analytical means. Therefore, (kinetic) Monte Carlo simulations have been a valuable tool in theoretical physics ever since their early stages, e.g. in solar cell simulations [1], [2]. By using pseudo-random numbers to mimic microscopic processes in an iterative fashion, complex systems can be modeled with various amounts of precision and detail. For example, modeling of disordered materials makes excessive use of Monte Carlo simulations [3]. Pronounced disorder can lead to the localization of particles at sites energetically located in the band gap. If localization prevails, electrical conduction and energetic relaxation may occur through phonon-assisted tunneling (hopping) between the sites [4]. Localization also occurs for bound electron-hole pairs (excitons), which dominate the properties of disordered optoelectronic devices [5].

II. Simulation of excitonic photoluminescence

We use Monte Carlo simulations to investigate the influence of mirror particles on low-temperature ($T = 5\,\mathrm{K}$) photoluminescence (PL) spectra of 2-dimensional semiconductors such as transition-metal dichalcogenide monolayers, e.g. $MoSe_2$ [6]. For the modeling, we use quadratic periodic boundaries. As a working hypothesis, the dielectric constant ε_{R} is set to 5.47 (calculated according to [7]). The site positions r_i are randomly distributed in space with a site density of $N = 6\,\mathrm{nm}^{-2}$. The site energies E_i are chosen randomly with an exponential probability density and an average value of $E_0 = 20\,\mathrm{meV}$ below the exciton energy E_{exc}. The value of E_0 is arbitrary, as it only scales the energy-axis as long as $E_0 \gg k_{\text{B}}T$. Excitons are generated at random sites according to a given spatial exciton density ρ_{exc}. They are modeled by aligned point-dipoles, which leads to a r^{-3}-dependency of the exciton-exciton interaction energy. Due to the periodic boundary conditions, mirror particles have to be taken into account when calculating energetic interactions. As the interaction energy is related to the exciton density, we choose the largest reported experimental exciton density ρ_{exc} of about $0.06\,\mathrm{nm}^{-2}$ in order to maximize the absolute value of the interaction energy [6]. After their generation, excitons hop from site to site with rates ν_{ij} according to the Miller-Abrahams formula [8]. Furthermore, Auger-like nonradiative exciton-exciton annihilation (EEA) is occurring for colliding excitons effectively, removing one exciton from the simulation. EEA is required in the simulation to prevent unphysical exciton-exciton agglomeration due to the dipole attraction, which results in an unphysical lineshape of PL spectra. Finally, excitons may recombine radiatively assuming a mean exciton lifetime of $\tau_0 = 1\,\mathrm{ns}$.

III. Influence of mirror particles

Theoretically, an elaborate summation in reciprocal space is necessary to include the infinite number of mirror particle energy contributions exactly. In hopping simulations though, very small interaction energies do not significantly alter the overall hopping dynamics. Therefore, we employ a simple real space summation covering the nearest mirror images of the original simulation box since the corresponding particles provide the highest contribution to the interaction energy. The total energy contribution E_{tot} of all particles to a site at location $\vec{r}$ at time t in the simulation is given by:

$$E_{\text{tot}}(\vec{r},t) = \sum_{i=1}^{n_{\text{exc}}(t)}{}' \sum_{j,k=-\gamma}^{\gamma} E_i\big(\big\|\Omega + \vec{n}(j,k)\cdot L_{\text{box}}\big\|\big)$$
$$\text{with } \Omega = \begin{cases} \vec{r}_i - \vec{r} & \gamma > 0 \\ \vec{r}_i - \vec{r} \mod\left(\frac{L_{\text{box}}}{2}\right) & \gamma = 0 \end{cases}, \tag{1}$$

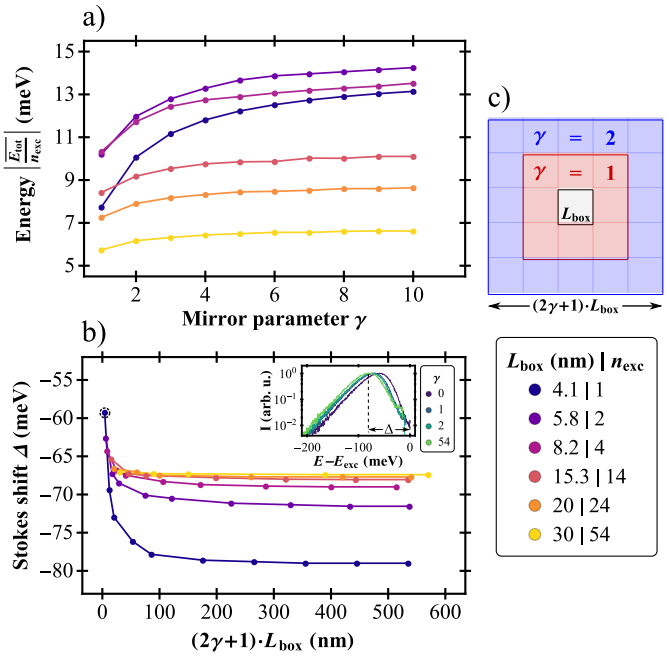

Fig. 1. a) The magnitude of the average mirror energy per exciton $|\overline{E_{tot}}/n_{exc}|$ is depicted for increasing γ values. Contributions in the original box ($j = k = 0$ in (1)) are excluded. b) The Stokes shift Δ as a function of the effective box length $(2\gamma + 1) \cdot L_{box}$: The dashed, black circle denotes the case of independent excitons without Coulomb interaction. The inset shows the PL spectra for $L_{box} = 4.1\,\mathrm{nm}$. c) A visualization of the original simulation box (grey) and the first two mirror sets (red and blue). The total number of mirror boxes for $\gamma > 0$ is $(2\gamma + 1)^2 - 1$.

where $n_{exc}(t)$ is the total number of particles present in the simulation at time t ($n_{exc}(0)$ is referred to as n_{exc}), E_i is the specific energy contribution of particle i, $\vec{n}(j,k) = j\binom{1}{0}+k\binom{0}{1}$ is a lattice vector. The integer γ specifies how many mirror sets of the simulation box (side length L_{box}) around the original one are taken into account (see Fig. 1c). The prime at the first sum in (1) denotes that we exclude the term $j = k = 0$, if $\vec{r_i} = \vec{r}$ to avoid self-interaction. In order to ensure that only closest particles interact in the original simulation box, the modulus is introduced for $\gamma = 0$. In this case, the largest possible distance between two particles is $L_{box}/2$ in each direction. Without the modulus, the interaction energy would yield a discontinuity at the edges of the box.

Fig. 1b depicts the Stokes shift Δ as a function of $(2\gamma+1)\cdot L_{box}$ for time-integrated PL spectra. The term $(2\gamma + 1) \cdot L_{box}$ corresponds to the total box length including all mirror sets (see Fig. 1c). The Stokes shift Δ is defined as the energy difference between absorption and emission maximum (see inset in Fig. 1b). In our case, the absorption maximum corresponds to the exciton transition of the isolated monolayer, which is set to $0\,\mathrm{meV}$. The box lengths in Fig. 1 are chosen according to the selected exciton density. The lowest number of excitons n_{exc} is 1 and determines the minimal cell size at this density. For small values of L_{box} and increasing γ, the magnitude of Δ is rising and Δ becomes constant for $(2\gamma + 1) \cdot L_{box} \geq 200\,\mathrm{nm}$. In this case, the Δ-difference between small and large L_{box} is about $11\,\mathrm{meV}$ at maximum (i.e. roughly half of the chosen energy scale E_0). This qualitatively different behavior arises because excitons may interact with all mirror particles, including their own. The magnitude of the average mirror interaction energy per exciton is shown in Fig. 1a. In order to compare the mirror contributions only, the terms $j = k = 0$ in (1) were excluded in the calculation. The attractive nature of the excitons lowers the energies of all other excitons in the simulation (which results in an effective red shift of the PL peak). This reduction enhances the overall hopping motion (e.g. the average diffusion length) and yields exciton agglomeration. However, due to nonradiative contributions, such as EEA, which are present in experiment and need to be considered during simulations, these clusters decay rapidly and do not visibly impact the PL lineshape. While n_{exc} rises proportional to L_{box}^2, the dipol-dipol energy decreases as r^{-3} with distance r. Therefore, the influence of mirror particles for a given value of γ is, on average, weaker for a larger L_{box} (an exception is $n_{exc} = 1$, see Fig. 1a). This yields an almost constant Δ when increasing γ at large L_{box}, which means that a smaller number of mirror sets is required to converge the PL spectra.

For the given exciton density, the Stokes shift Δ converges with the number of mirror sets γ for values of $(2\gamma+1)\cdot L_{box} \geq 200\,\mathrm{nm}$ at a constant box length. However, this is misleading as long as the box size is not converged at the same time. The particle nature of the excitons results in correlated distances between the particles of the original box and of the mirror sets for low exciton numbers. In order to statistically remove these unphysical correlations, about 50 and more excitons are required in the original box, which imposes constraints of the minimum required box length to obtain physically meaningful results.

IV. Conclusion

Periodic boundary conditions require the consideration of mirror particles. In order to obtain converged PL spectra using a simple real space summation, values of $(2\gamma + 1) \cdot L_{box} \geq 200\,\mathrm{nm}$, with the box length L_{box} and the number of included mirror sets γ, and about 50 excitons are required.

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