Microscopic theory of the optical properties of colloidal graphene quantum dots

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We present a microscopic theory of electronic and optical properties of colloidal graphene quantum dots (CGQDs). The single-particle properties are described in the tight-binding model based on the $p_z$ carbon orbitals. Electron-electron screened Coulomb direct, exchange, and scattering matrix elements are calculated using Slater $p_z$ orbitals. The many-body ground state and excited states are constructed as a linear combination of a finite number of excitations from the Hartree-Fock (HF) ground state (GS) by exact diagonalization techniques. HF ground states corresponding to semiconductor, Mott-insulator, and spin-polarized phases are obtained as a function of the strength of the screened interaction versus the tunneling matrix element. In the semiconducting phase of a triangular CGQD, the top of the valence band and the bottom of the conduction band are found to be degenerate due to rotational symmetry. The singlet and triplet exciton spectra from the HF GS are obtained by solving the Bethe-Salpeter equation. The low-energy exciton spectrum is predicted to consist of two bright-singlet exciton states corresponding to two circular polarizations of light and a lower-energy band of two dark singlets and 12 dark triplets. The robustness of the bright degenerate singlet pair against correlations in the many-body state is demonstrated as well as the breaking of the degeneracy by the lowering of symmetry of the CGQD. The band-gap renormalization, electron-hole attraction, fine structure, oscillator strength, and polarization of the exciton are analyzed as a function of the size, shape, screening, and symmetry of the CGQD. The theoretical results are compared with experimental absorption spectra.

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I. INTRODUCTION

There is currently interest in the optical properties of graphene [1–20] and graphene-based nanostructures, carbon nanotubes [21–31], nanoribbons [32–35], and graphene quantum dots [36–58]. Graphene quantum dots are interesting because their electronic [36–45], magnetic [42,43,46–55], and optical properties [51,55,57,58] can be potentially engineered by controlling their size, shape, edge character, number of layers, and carrier density. In particular, Li and co-workers described recently a class of colloidal, solution processable graphene quantum dots (CGQDs) with a well defined structure [59–63]. Two classes of dots, with $N = 168$ and 132 atoms, were obtained and the absorption and emission of solutions containing CGQDs were measured [61]. The number of atoms in each dot was determined from mass spectrometry, while the symmetry was inferred through the solution chemistry and infrared vibrational spectra. Since the CGQDs are suspended in solution, whose dielectric constant can be tuned, their optical response can be studied as a function of their size and shape, as well as the strength of the Coulomb interactions. Indeed, optical absorption spectra reveal a clear dependence of the position of the absorption edge on the number of atoms [59–62]. The fluorescence and phosphorescence spectroscopy [61] shows the existence of a gap between emission and absorption spectra interpreted in terms of the energy difference between the singlet and triplet exciton states.

The GCQD with $N = 168$ atoms in vacuum was recently analyzed theoretically by Schumacher [64] using the time-dependent density functional theory (DFT) approach. The numerical simulation revealed the existence of a bright-singlet exciton doublet in a band of dark-triplet and singlet states.

Here we present a microscopic theory of the optical properties of colloidal graphene quantum dots based on a combination of the tight-binding (TB) description of the $p_z$ single-electron states and screened electron-electron interactions treated by exact diagonalization methods in the space of multipair excitations out of the Hartree-Fock (HF) ground state. We find the semiconducting, Mott-insulator, and spin-polarized HF ground states as a function of the strength of the Coulomb interaction. In the semiconductor phase we describe a universal form of the exciton spectrum, with the two bright-singlet exciton states and a band of two dark-singlet and 12 triplet exciton states at low energy, in agreement with the results of Schumacher. We determine the bright-singlet dark-triplet exciton splitting and relate the degeneracy of the bright exciton states to the symmetry of the quantum dot. The effect of the reduction of size and the removal of symmetry on the exciton spectrum is investigated by comparing the $N = 168$ and 132 CGQDs. The theoretical absorption spectra are compared with experiment.

The paper is organized as follows. In Sec. II we describe the structure, model Hamiltonian, and the TB-HF-configuration interaction (CI) method. In Sec. III we present a symmetry analysis of the band-edge exciton spectra of the triangular $N = 168$ CGQD and numerical results for $N = 168$ and 132 CGQDs. In Sec. IV we discuss the effect of screening on optical properties and compare theoretical absorption spectra with the experimental data. Section V contains conclusions.
II. THE MODEL

The CGQDs C132 and C168 [59–63] are modeled as two-dimensional clusters of carbon atoms, depicted as blue circles, forming the perfect honeycomb lattice with the bond length \( a_0 = 0.142 \, \text{nm} \), as shown in Fig. 1. As seen in the figure, the \( N = 132 \) atom graphene quantum dot is obtained by cutting out the upper corner consisting of 36 carbon atoms from the dot with \( N = 168 \) atoms. The \( N = 132 \) CGQD is smaller and does not have the rotational symmetry of the C168 molecule. For both structures, we assume hydrogen passivation and no edge reconstruction [53].

Building on our earlier work [44,52,53,58], we assume that the mobile electrons occupy the states of the \( p_z \) band composed of the spin-degenerate \( p_z \) orbitals, one per atom. As a result, the charge-neutral CGQD with \( N \) atoms carries \( N \) electrons.

We start by describing the motion of a single electron in a lattice of positively charged ions. Out of six electrons belonging to each carbon atom, five are strongly bound, forming the bonds in the plane of the CGQD and partially shielding the Coulomb potential of the carbon nucleus. We expand the wave function in the basis of orthogonalized atomic shielding the Coulomb potential of the carbon nucleus. We forming the bonds in the plane of the CGQD and partially belonging to each carbon atom, five are strongly bound, in a lattice of positively charged ions. Out of six electrons this way reconstruction [53].

For the full HF treatment, all direct, exchange, and scattering Coulomb matrix elements are computed numerically by approximating the \( p_z \) orbitals with Slater functions for up to second-nearest-neighbor atoms [44,52,53,58] while for atoms at greater distances, the matrix elements are approximated by matrix elements corresponding to classical point-charge interactions. Coulomb interactions are assumed to be screened by the effective dielectric constant \( \kappa \) with contributions from both the \( \sigma \) electrons of graphene and the solvent in which the dots are suspended. The Hamiltonian contains two energy scales, the hopping matrix element \( t \) and the Coulomb interactions screened by the effective dielectric constant \( \kappa \). The two energy scales determine the electronic properties of CGQDs.

A. Hartree-Fock approximation

The full interacting Hamiltonian for the \( N \)-atom CGQD with \( N \sim 10^2 \) cannot be diagonalized exactly. Thus we start by solving the Hartree-Fock problem first and treating the interactions among HF quasiparticles second. The HF Hamiltonian is obtained from the full Hamiltonian by replacing the two-body scattering terms with the single-particle scattering from the potential of the mean-field density matrix, which becomes

\[
H_{\text{MF}} = \sum_{i \in \sigma} h_{ii} c_{i\sigma}^+ c_{i\sigma} + \sum_{i \in \sigma, j \in \sigma'} \sum_{\delta} \langle i j | V | k \rangle \delta_{\sigma \sigma'} (c_{j\sigma'}^+ c_{k\delta} + c_{k\delta}^+ c_{j\sigma'}) c_{i\sigma}.
\]

where we introduced the effective hopping element \( \tilde{t}_{ij} = t_{ij} - \sum_{k \in \sigma} \langle i k | V | j \rangle \) and \( \langle i j | V | k \rangle \) = \( \rho_{j \sigma k \delta} \) are the elements of the density matrix. The HF operators are defined as linear combinations of atomic operators \( b_{2\sigma}^+ = \sum_{i \in \sigma} B_{2\sigma i} c_{i\sigma}^+ \) that diagonalize the converged HF Hamiltonian as

\[
\hat{H} = \sum_{i \in \sigma} \sum_{\sigma} \tilde{t}_{ii} c_{i\sigma}^+ c_{i\sigma} + \sum_{i \in \sigma, j \in \sigma'} \sum_{\delta} \langle i j | V | k \rangle \delta_{\sigma \sigma'} (c_{j\sigma'}^+ c_{k\delta} + c_{k\delta}^+ c_{j\sigma'}) c_{i\sigma}.
\]
\[ \sum_{p,q=1}^{N} \sum_{\sigma} \epsilon_{p\sigma} b_{p\sigma}^\dagger b_{q\sigma}. \] The HF energies are composed of two parts: \( \epsilon_{p\sigma} = E_{p\sigma} + \Sigma(\sigma p\sigma) \). The single-particle part, \( E_{p\sigma} \), originates from the single-particle tight-binding part of the Hamiltonian \( H_{\text{MF}} \), and the self-energy, \( \Sigma(\sigma p\sigma) = \sum_{q=1}^{N-1} \langle 2(pq|V_{\text{HF}}|qp) - \langle pq|V_{\text{HF}}|pq \rangle \rangle \), accounts for all direct and exchange interactions of the electron in the HF orbital \( p \) with all other electrons filling the valence band. Note that in the above equation the Coulomb elements in the basis of HF orbitals are obtained by rotating the elements \( |i\rangle |j\rangle \) in \( |p\rangle |q\rangle \) defined in the basis of localized orbitals [Eq. (2)]:

\[ \langle pq|V_{\text{HF}}|rs \rangle = \sum_{i,j,k,l} B_{p,i} B_{q,j} B_{r,k}^* B_{l,l}(ij|kl\rangle. \]

One can further simplify the problem from the full HF approximation and treat the system in the Hubbard \( U \) approximation. Then, instead of using the full Hamiltonian, one would eliminate all Coulomb interactions except for the on-site \( U_i = \langle ii|V|ii \rangle \) terms and create Hubbard \( U \) quasiparticles.

**B. Interaction of HF quasiparticles**

The rotation of the single-particle basis, defined by the HF procedure, diagonalizes the mean-field Hamiltonian \( H_{\text{MF}} \) [Eq. (3)], but not the full Hamiltonian given in Eq. (1). To proceed further, we now rotate the full Hamiltonian into the HF basis. Expressing the operators \( c_{i\sigma}^+ \) and \( c_{p\sigma} \) in Eq. (1) in terms of the HF creation (annihilation) operators \( b_{p\sigma}^\dagger \) and \( b_{p\sigma} \) as

\[ c_{i\sigma}^+ = \sum_{p=1}^{N} B_{p,i}^* b_{p\sigma}, \]

and rewriting the hopping elements \( \tau_{ij} \) in terms of the HF energy levels using Eq. (3), we obtain the full Hamiltonian in the basis of the HF quasiparticles in the form

\[ H_{\text{QD}} = \sum_{p,q=1}^{N} \sum_{\sigma} \epsilon_{p\sigma} b_{p\sigma}^\dagger b_{q\sigma} + V_{\text{MF}}^{pq} b_{p\sigma}^\dagger b_{q\sigma} + \frac{1}{2} \sum_{p,q,r,s,\sigma,\sigma'} \langle pq|V_{\text{HF}}|rs \rangle b_{p\sigma}^\dagger b_{r\sigma}^\dagger b_{r\sigma'} b_{s\sigma'}, \]

where

\[ V_{\text{MF}}^{pq} = \sum_{r,\sigma'} n_{r,\sigma'} \langle \langle pr|V_{\text{HF}}|qr \rangle - \delta_{\sigma\sigma'}(pr|V_{\text{HF}}|qr) \rangle. \]

Here \( n_{r,\sigma'} \) is the number operator determining the occupation of the HF level \( r \) by a spin-\( \sigma' \) electron.

**C. Correlations via multipair excitations from the HF state**

We now proceed to include electronic correlations as interactions of HF quasiparticles using the CI method. The configuration-interaction step involves creating a basis set, including the HF state \( |HF_{gs}\rangle \) and all the excitations up to the selected number of quasiparticles, constructing the matrix of the Hamiltonian \( H_{\text{CI}} \) [Eq. (6)] in this basis, and diagonalizing this matrix numerically. As a result, one obtains correlated eigenstates \( \Phi_{\nu} \) of the form

\[ |\Phi_{\nu}\rangle = k_0 |HF_{gs}\rangle + \sum_{i,j,\sigma} k_{ij}^{(1)} |i\sigma; j\sigma\rangle + \sum_{i,j,k,l,\alpha,\gamma} k_{ijkl}^{(2)} |i\alpha, j\gamma; k\alpha, l\gamma\rangle + \cdots. \]

Here \( |p\sigma; q\sigma\rangle = b_{p\sigma}^\dagger b_{q\sigma} |HF_{gs}\rangle \) are the single-pair excitations that create an electron-hole pair at states \( p-q \), conserving the total projection of the spin. Similarly, \( |p\sigma_1, q\sigma_2; r\sigma_1, s\sigma_2 \rangle \) are the two-pair excitations and so on.

In particular, the HF ground state itself is corrected by contributions from multipair excitations. The corrected ground state will then be expressed as \( \Phi_0 \).

**D. Absorption spectra**

The absorption spectrum of a photon with energy \( \omega \) is obtained from Fermi’s golden rule:

\[ A(\omega) = \sum_{\nu} W_{\nu} \langle \Phi_{\nu} | \hat{P}^\dagger | \Phi_{\nu} \rangle \delta(E_{\nu'} - E_{\nu} - \omega), \]

where \( E_{\nu}, E_{\nu'} \) are the energies of the initial and the final state participating in the absorption, \( \hat{P} = \sum_{p,q} d(p,q) b_{p\sigma}^\dagger b_{q\sigma} \) is the polarization operator adding a pair excitation while annihilating a photon, and \( W_\nu \) is the probability that the initial many-body state \( \nu \) is occupied.

We will now elaborate on the dipole element \( d(p,q) \) appearing in the polarization operator, which is described in terms of atomic orbitals as

\[ d(p,q) = \sum_{i=1}^{N} \sum_{j=1}^{N} B_{p,i}^* B_{q,j} \langle \delta | \vec{\varepsilon} \cdot \vec{r} | \rangle, \]

where \( \vec{\varepsilon} \) is the polarization of light. We first need to evaluate the dipole element in the basis of atomic \( p_r \) orbitals. Using the orthogonality of the orbitals, and setting all terms to zero except for the on-site and the NN terms, we get the dipole element between \( p_r \) orbitals as [58,65]

\[ (i| \vec{\varepsilon} \cdot \vec{r} | j) = D_{ij} \vec{\varepsilon} \cdot (\vec{R}_j - \vec{R}_i) (1 - \delta_{ij}) + \vec{\varepsilon} \cdot \vec{R}_i \delta_{ij}, \]

where the coefficient \( D_{ij} = \int d\vec{r} \phi_i^*(\vec{r}) \vec{\varepsilon} \phi_j(\vec{r} - \vec{R}_i) \) is computed using the Slater \( p_z \) orbitals. In our calculations, we include NN and NNN elements which are calculated as \( D^{\text{NN}} = 0.3433 \) and \( D^{\text{NNN}} = 0.0873 \) in units of nearest neighbor distance, respectively.

**III. ELECTRONIC AND OPTICAL PROPERTIES OF N = 168 COLLOIDAL GRAPHENE QUANTUM DOT**

In this section, we apply the TB-HF-CI methodology to the electronic states and absorption spectrum of \( N = 168 \) CGQD.

**A. Rotational symmetry**

The triangular \( N = 168 \) CGQD is rotationally symmetric and exhibits all point symmetries of the graphene sheet. The three symmetry axes, shown in red, divide the CGQD into three segments, \( A, B, \) and \( C \), with 56 atoms each. We assign atomic index \( j_{\beta} (\beta = A) \) to atoms in segment \( A \). Equivalent atoms in
segments B and C, related by a rotation of $\pm \alpha = 2\pi/3$, are shown in Fig. 2.

To proceed further we assign values to atomic segments (A, B, C) as $\{0,1,2\}$. Next, by rotating each atomic orbital group $(j_A, j_B, j_C)$, we construct new basis vectors

$$\Psi^m_j = \frac{1}{\sqrt{3}} (|j_0\rangle + e^{i(m 2\pi/3)} |j_1\rangle + e^{i(m 2\pi/3)} |j_2\rangle),$$

with $m = \{0,1,2\}$.

After rotating to the new basis, we find the TB Hamiltonian block diagonal for each $m = \{0,1,2\}$ subspace and, upon diagonalization of the TB Hamiltonian, obtain the single-particle energy levels with eigenvalue index $\nu$ and quantum number $m$, shown in Fig. 3(a). We find the conduction band minimum (CM) and valence band maximum (VM) of the C168 molecule to be degenerate due to the degeneracy of the $m = 1$ and $m = 2$ subspaces, which is a result of the fact that $e^{i 2\pi/3} = (e^{i \pi/3})^2 = (e^{-i \pi/3})^2$. The degeneracy of these levels can be linked to the valley degeneracy of graphene.

We now relate the triangular symmetry to the dipole elements and optical selection rules. Expanding the rotationally invariant eigenvectors $|v,m\rangle$ in terms of localized orbitals, Eq. (12), and assuming circular polarization of light $\epsilon_\pm$, after lengthy algebra, we find that the dipole elements between the CM/VM levels satisfy the selection rule

$$\langle v',m'|\vec{r}\cdot \vec{r}|v,m\rangle = \delta_{m',m\pm 1} C_{m,m',v,v'},$$

where $C$ is a constant determined numerically.

Arrows in Fig. 3(a) show the optical transitions with a finite matrix element while Fig. 3(b) shows all possible transition energies along with their dipole matrix elements, with vertical transitions indicated by a gap from the next shell. However, the lack of dipole moments for some of the transitions between the higher lying $m = \{1,2\}$ states with the $m = 0$ levels visible in Fig. 3(b) is due to the weak overlap of the wave functions and is unrelated to the symmetry.

Below we will analyze the structure of the lowest-energy shell in absorption in the interacting CGQD.

### B. Band-edge exciton

Let us now describe the characteristic spectrum of band-edge excitons on the lowest-energy shell. We relabel the two topmost valence band states as $|v1,v2\rangle$ and two lowest-energy conduction band states as $|c1,c2\rangle$.

We start by filling up all the VB TB orbitals with spin-up and spin-down electrons and forming the HF ground state $|HF_{gs}\rangle$ as shown in Fig. 4(a). Next, the excitations $|p,q\rangle = b^+_p |HF_{gs}\rangle$ are created. The $\Delta m = \pm 1$ optically active excitations are shown in Fig. 4(b). There is only one electron-hole pair with $\Delta m = +1$ and one with $\Delta m = -1$ for a given spin of an excited electron. The energy of each pair, $E_{p,q} = \epsilon_p - \epsilon_q + \Sigma(p) - \Sigma(q) - \langle pq | V_{HF} | qp \rangle$, is given by a difference.
in single-particle energies and self-energies $\Sigma$ between the
electron and hole and by the electron-hole attraction.

With two possible $\Delta m = \pm 1$ states and two possible
spin directions, there are four exciton states, as shown
on the right-hand side of Fig. 5(a). There is one sin-
glet and one triplet state with $S_z = 0$ for each $\Delta m = \pm 1$ state
given as $|p,q,S/T\rangle = \frac{(b_p^\dagger)^{\sigma_p} (b_q^\dagger)^{\sigma_q}}{\sqrt{2}} |\text{HF}_{\text{gs}}\rangle$. The en-
ergy of the singlet and triplet, $E_{p,q,S/T} = \epsilon_p - \epsilon_q + \Sigma(p) - \Sigma(q) - \langle p q | V_{\text{HF}} | q p \rangle + \langle p q | V_{\text{HF}} | p q \rangle \pm \langle p q | V_{\text{HF}} | p q \rangle$, differs
by twice the exchange, which pushes the singlets up in energy.
A similar analysis is carried out for the two $\Delta m = 0$ [Fig. 4(c)]
dark configurations, as shown on the left-hand side of Fig. 5(a).
Two $\Delta m = 0$ configurations of each total spin component
interact, and thus their energy is renormalized. The final
spectrum of the band-edge excitons is shown in the middle
column (Full CI) of Fig. 5(a). We find two bright degenerate
singlet exciton states and a band of two dark-singlet and four
dark-triplet exciton states at lower energies. If we count all
possible $S_z$ configurations, the low-energy band consists of two
dark-singlet and 12 dark-triplet states. By comparing Fig. 5(a)
obtained from full HF quasiparticles and Fig. 5(b) obtained
from Hubbard $U$ quasiparticles in the semiconductor regime,
we see that the separation of the degenerate bright singlets from
the forest of dark singlets and triplets is robust. However, the
ordering of the levels in the dark region changes from Hubbard
$U$ to full HF due to the inclusion of exchange interactions
which drive the lowest excited state from a singlet to a
triplet.

C. Numerical results

We now turn to the numerical analysis of the absorption
spectrum. We start with a comparison of the TB and fully
self-consistent Hartree-Fock energy spectra. Figure 6 shows
the tight-binding and fully self-consistent Hartree-Fock energy
levels for $\kappa = 5$, $t = -3.0$ eV, and $t_2 = -0.1$ eV, both
normalized to the middle of the energy gap. We see that
the HF energy spectrum, renormalized by the self-energy,
resembles closely the tight-binding spectrum. In particular,
the degeneracy of VB maximum (VBM) and CB minimum
(CBM) is preserved. The main differences between spectra
are the breaking of electron-hole symmetry and changes in the
electron bandwidth, which are expected in HF.

By minimizing the energy of the ground state through
the self-consistent HF procedure, we obtain the quasiparticle
states and energy levels as well as the interactions between HF
quasiparticles. Next, we compute the ground and excited states
and the absorption spectrum using the TB-HF-CI approach.
This allows us to discuss the robustness of the band-edge excitons and absorption spectrum discussed above.

Figure 7 shows the evolution of the low-energy excitonic spectrum associated with the degenerate VBM/CBM states. The topmost panel shows the absorption spectrum of the noninteracting CGQD. The second panel shows the absorption in the TB-HF approximation. The self-consistent HF approach protects the rotational invariance of the $m = \{0,1,2\}$ subspaces but blueshifts the energy gap due to differences in self-energy of the electron and the hole, as expected.

The third panel of Fig. 7 shows the band-edge exciton spectrum calculated from the HF ground state. We see that the inclusion of electron-hole attraction, exchange, and electron-hole correlations redshifts the absorption spectrum and separates in energy the singlet and triplet excitons. The two bright excitons remain degenerate, and a band of dark singlets and triplet exciton states appears at lower energy. The last row in Fig. 7 shows the absorption spectrum calculated using renormalized ground and excited states obtained after the inclusion of all possible configurations with up to four pairs within the limited Hilbert space of four VB and four CB HF states. The renormalization of the energy of the ground and excited triplet states with the number of excited pairs is shown in the inset. We see that the inclusion of multipair excitations renormalizes both the ground state and the excited states, but does not significantly shift the transition energies nor does it remove degeneracies or change the structure of the absorption spectra. We conclude that the absorption spectrum obtained from an exciton excited out of a HF ground state is a good approximation for a semiconductor CGQD. Below we will discuss how the absorption depends on the tunneling matrix element and on screening of electron-electron interactions.

IV. EFFECTS OF SCREENING $\kappa$ AND TUNNELING $t$

The ground state properties depend strongly on the values of the strength of screening and the amplitude of the hopping term. Previous work on the ground state properties of graphene [66–69] suggest that for strong Coulomb interactions, or small values of $\kappa$, there exists a transition from a semimetallic, weakly interacting phase to a Mott-insulating, strongly correlated phase. Below we discuss the phase diagram of C168 as a function of $\kappa$ and $t$. Figure 8(a) shows the energy of the full HF and Hubbard $U$ ground states for the spin-polarized, $S_z = N/2$, and spin-unpolarized, $S_z = 0$, C168 as a function of $\kappa$ for $t = -4.2\ eV$. We see that, compared to the spin-polarized case, the spin-unpolarized phase is the ground state for all $\kappa$ down to $\kappa = 1.4$ in full HF while the spin-polarized state is predicted as the ground state at $\kappa < 1.4$ using the full HF approximation. Figure 8(b) shows the calculated average density matrix element $\rho_{\sigma} = \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$ for $i,j$ nearest neighbors, averaged over all pairs for a spin-unpolarized ground state as a function of $\kappa$. The density matrix element shows the probability of having two electrons with the same spin on nearest-neighbor orbitals. For large $\kappa$ we find $\rho_{\sigma} = 0.26$, i.e., the value for the HF state of bulk graphene [56]. The local values of $\rho_{\sigma}$ of course differ from the bulk value at the edges even at the high-$\kappa$ range. Using full HF, as $\kappa$ decreases, we see the onset of the phase transition at around $\kappa < 1.8$. For $\kappa < 1.8$ the ground state departs from the semiconducting state of graphene and becomes a Mott insulator, with spin-up electrons on lattice $A$ and spin-down electrons on lattice $B$. Increasing the magnitude of the hopping
parameter $t$ results in a phase transition at lower $\kappa$ values. However, in Hubbard $U$ we do not observe a pronounced spin separation compared to full HF.

We now discuss the evolution of the exciton spectra as a function of $t$ and $\kappa$ in the semiconducting phase. Figure 9(a) presents the results of the calculated energy of the bright degenerate singlets and $\Delta_{S/T}$ while the separation between the bright singlet and the lowest-energy dark triplet as a function of $t$ and $\kappa$ is given in Fig. 9(b). We see that the energy of the bright singlets weakly depends on $\kappa$ but varies with tunneling matrix element $t$ from $\sim 1$ eV for $t = -2$ eV to $\sim 2$ eV for $t = -4.2$ eV. The bright-singlet–dark-triplet separation $\Delta_{S/T}$ is due to electron-electron interactions and is influenced by the dielectric constant $\kappa$ rather than the hopping element $t$. For $t = -4.2$ eV, $\Delta_{S/T}$ varies from 0.15 eV for $\kappa \sim 6$ to 0.35 eV at $\kappa \sim 2$.

We now compare the calculated absorption spectra with experiment. Figure 10(a) shows the measured [61] and calculated absorption spectra for $\kappa = 5.0$ and $t = -4.2$ eV. We have used Gaussian broadening in continuous plots and added 10% of the oscillator strength of the brightest peak to the dark singlets since they may contribute to absorption if the symmetry is broken due to, e.g., charge and spin fluctuations in the surrounding fluid. We see that the measured absorption spectra show an absorption threshold around $E = 1.8$ eV, a peak at $E = 2.25$ eV, and a reduced absorption strength up until $E = 3$ eV. Our preliminary interpretation assigns the peak in the measured absorption spectrum at $E = 2.25$ eV to the bright-singlet excitons while we predict the absorption threshold as due to dark singlets, which dictates the choice of $t$ and $\kappa$. The calculated absorption spectrum can reproduce the position of the absorption peak due to bright excitons followed by a gap. However, the singlet-triplet splitting is significantly underestimated when compared with experiment.

A. Effect of reduced size and symmetry: $N = 132$ colloidal graphene quantum dot

We now proceed to discuss the effect of reduced size and symmetry on the optical properties of CGQDs. C132, shown in Fig. 1, can be obtained from C168 by cutting off one corner, and hence it lacks $C_3$ symmetry. As a result, the degeneracy of the top of the valence band and bottom of the conduction band is removed and there are nonzero dipole elements between all CB and VB levels. The degeneracy of the high-energy bright singlets is removed and the low-energy dark singlets acquire nonzero oscillator strength. Figure 10(b) shows the calculated and measured absorption spectrum for C132. Due to reduced size and increased confinement of Dirac fermions, the C132 absorption spectrum is blueshifted compared to C168, both in experiment and in theory. The calculated spectra show the splitting of the bright-singlet exciton peak. The splitting is not visible in experiments on ensembles of CGQDs in a fluid. Again, the singlet-triplet splitting is underestimated compared to experiment.

V. CONCLUSIONS

We presented a microscopic theory of electronic and optical properties of colloidal graphene quantum dots (CGQDs) based on the tight-binding, Hartree-Fock, and configuration interaction approaches. The low-energy exciton spectrum is predicted to consist of two bright-singlet exciton states corresponding to two circular polarizations of light and a lower-energy band of two dark singlets and 12 dark triplets. The effects of symmetry, size, shape, screening, band-gap renormalization, electron-hole correlations, and many-body corrections are analyzed. The theoretical results are compared with experimental absorption spectra. While a good overall agreement is found, the singlet-triplet splitting is underestimated. Future theoretical work should improve on the screening of the Coulomb interaction and the effects of lattice vibrations on the absorption and emission spectra. Future
experimental work should attempt to identify the degenerate singlet states in C168 and their splitting in C132 colloidal graphene quantum dots.

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