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Exact diagonalization of Hubbard models for the optical properties of single-wall carbon nanotubes

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\textbf{Abstract.} Excitonic states of single-walled carbon nanotubes (SWNTs) have usually been calculated using many-body perturbation theories or mean field approaches because a large number of sites cannot be considered within an exact diagonalization (ED) calculation based on the Hubbard model. We use a small crystal approach and show that, for the $\pi$ structure of nanotubes, an ED calculation is possible. We apply this approach to small-diameter SWNTs and the results show that a crossing of the first bright state with the second excited states occurs when $U$, the correlation parameter of the Hubbard model, equals $4t$, where $t$ is the hopping integral. Two or three strong two-photon absorption (TPA) states are found at energies above the first bright state for $U/t \leq 3$. Beyond this value, these states become relevant for TPA below the first bright state. A number of dark states are always calculated below the first bright state at energies that, in the intermediate coupling regime, are of the order of tens to hundreds of meV. This result seems to be consistent with recent experiments.

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1. Introduction and method

In recent years, a considerable amount of experimental and theoretical work has investigated the electronic correlation effects in single-walled carbon nanotubes (SWNTs) [1]. It is now generally accepted that, because of the poor dielectric screening due to the strong quantum confinement in 1D, Coulomb interactions between \( \pi \) electrons play a key role in accounting for several findings, such as the large exciton binding energy, the blueshift of the single-particle transition energies and the so-called ratio problem, namely the ratio of the second to the first optical transition, which is found to be less than 2, the value predicted by the tight-binding (TB) picture in the large diameter limit, when correlation is switched on [2]–[9]. Experiments have confirmed the excitonic nature of one- and two-photon spectra of SWNTs [10]–[17]. Recently, theoretical investigations have confirmed the excitonic nature also for metallic SWNTs although with lower binding energy [1, 18, 19]. Theoretical results have helped in clarifying many issues related to excitonic spectra. For example, the GW–Bethe–Salpeter equation (GW–BSE) initially adopted by Louie [3, 8], Molinari [5] and Avouris [6], introduced electronic correlations with a many-body perturbation theory in order to overcome the limits of mean-field-based LDA-DFT calculation, and determined the excitonic level structure with the presence of one dark state below the bright one, which is consistent with the low fluorescence yield of carbon nanotubes. On the other hand, single-configuration interaction Hartree–Fock (SCI-HF) calculations [7, 20] considered the \( e-e \) interaction with an explicitly parametrized semi-empirical Parriser–Parr–Pople (PPP) Hamiltonian for \( \pi \) electrons, and found the presence of more than one dark state below the bright one. Analogous results have been found by Ando considering a \( k \cdot p \) approximation [21].

In this work, we report a strategy for a full many-body approach of the excitonic spectra of SWNTs, which has not been used so far in the investigation of optical excitations in carbon nanotubes. The calculations are based on the Hubbard model Hamiltonian [23] for \( \pi \) electrons,

\[
H^{2D} = -t_{\pi} \sum_{\langle i,j \rangle,\sigma} \left( c_{i,\sigma}^{\dagger} c_{j,\sigma} + c_{j,\sigma}^{\dagger} c_{i,\sigma} \right) + U \sum_i n_{i,\uparrow} n_{i,\downarrow},
\]

where \( i \) and \( j \) are site indices, \( \langle i, j \rangle \) are all pairs of first nearest-neighbour sites, \( c_{i,\sigma}^{\dagger} \) and \( c_{i,\sigma} \) are electron creation and annihilation operators, \( n_{i,\sigma} = c_{i,\sigma}^{\dagger} c_{i,\sigma} \) is the number of electrons on site \( i \) with spin \( \sigma \), and \( t_{\pi} \) and \( U \) are positive interaction constants for the hopping amplitude between adjacent sites and the on-site Coulomb repulsion between two electrons with opposite spins. Values of the correlation parameter \( U \) have to be interpreted considering that the on-site Coulomb interaction is an effective parameter that additionally takes into account neighbour interactions (\( V_n \) terms in extended Hubbard models, \( V_1 \) for the first nearest neighbour) and, in particular, its value for half-filled systems can be considered equivalent for non-small values of the interactions, to \( U - V_1 \). Therefore the \( U \) parameter must be considered as an effective on-site Coulomb interaction that considers also longer range interactions, which are usually important for obtaining exciton energies [21].

Our method exploits the small crystal approach (SCA) ([24] and references therein; [25, 26]), which considers finite-size quantum lattice models with few sites and appropriate boundary conditions. With this method, we probe a finite number of points in the first Brillouin zone and, by including among these points the van Hove singularities, one can calculate the optical properties of SWNTs. The method was recently applied to TB calculations of
Figure 1. Brillouin zone sampling with a $2n$-site zigzag $(n, 0)$ NT cluster: by applying azimuthal PBCs ($\mu$ even, $k_z = 0$) points (empty circles) are sampled, by applying azimuthal APBCs ($\mu$ odd, $k_z = 0$) points (black squares) are sampled. $\mu$ and $k_z$ are the azimuthal quantum number and the axial quantum number, respectively, while $|T|$ gives the length of the SWNT unit cell along the nanotube axis.

double-walled nanotubes (DWNTs) with orientation-dependent inter-tube interactions, which allowed us to show that important symmetry breakings are introduced by the interaction [27].

We choose a multi-particle basis set with $S_z = 0$ for a half-filled system with conserved particles number, since the linear optical properties are to be found in this configuration space, although there are no particular restrictions on the total spin quantum number used for obtaining the basis set. The electronic excitation spectrum at the sampled $k$ points is obtained with an exact diagonalization (ED) of the Hubbard Hamiltonian and the spectral function from the velocity operator is calculated using the lowest-energy eigenstates [25, 31, 32]. It is well known that the ED of the Hubbard model applied to systems with more than 16 sites is a challenging problem, because the number of basis states grows exponentially as $4^N$ with the number of sites $N$ in the system. Our approach allows one to use the essential number of sites, which can also be reduced by exploiting the symmetry of the system under investigation.

A single unit cell with periodic boundary conditions (PBCs) allows us to sample the van Hove singularities of zigzag $(n, 0)$ nanotubes. These points are found at the centre of each $\mu$th cutting line, i.e. at $k_z = 0$, as shown in figure 1, where $\mu$ is the azimuthal quantum number and $k_z$ is the axial quantum number, which label SWNT BZ points [33, 34]. By including
Figure 2. Zigzag (4,0) (upper) and (5,0) (bottom) clusters with 2n sites and azimuthal boundary conditions to sample \((\mu, k_z = 0)\) points in the nanotube BZ. Points with the same colour refer to the same index site.

only these points into a model calculation, one can obtain the same essential spectral profile that would be obtained from a calculation over the whole nanotube BZ, since the NT optical absorption spectrum is dominated by the joint density of states (JDOS) [27]. The number of sites in a zigzag SWNT unit cell is \(4n\), where \(n\) is their chiral index; thus the calculation is very challenging, even for the smallest diameter tubes. However, it is possible to reduce the cluster size to \(2n\) by considering the presence of symmetry elements. We considered semiconducting-like (4,0) and (5,0) nanotubes, although these tubes are hypothetical and the (5,0) is thought to be a metal, considering the \(\sigma-\pi\) hybridization [28]–[30], because in this case the Hubbard matrix can be fully stored in an ordinary cluster computer. Therefore, the following results show the applicability of the methodology to the investigation of the excitonic properties of nanotubes and give a qualitative insight into the relevant optoelectronic properties of nanotubes, as a function of the Hubbard parameters. Further reduction of the cluster sizes, on the basis of their symmetries, will allow us to study larger nanotubes. For the (4,0) and (5,0) nanotubes, we considered the presence of an order-two rotation axis perpendicular to the SWNT axis and centred on a C–C bond for (4,0) or at the centre of a graphene hexagon for (5,0), respectively (figure 2).

By applying PBCs, i.e. a hopping integral with a phase factor \(\phi = 0\), along the azimuthal direction, one samples the points at \(k_z = 0\) that belong to cutting lines with even \(\mu\), whereas with anti-periodic boundary conditions (APBCs) \((\phi = \pi)\), one samples those belonging to odd \(\mu\) (figure 1).

The absorption spectrum can be computed with the sum-over-states (SOS) method,

\[
I(E) = \sum_{m} |\langle \psi_{m} | v_{2D}^{\sigma} | \psi_{GS} \rangle|^2 \delta (E + E_{GS} - E_{m}),
\]

where \(E_{GS}\) is the ground-state (GS) energy of the system and \(E_{m}\) is the energy of any other eigenstate \(|\psi_{m}\rangle\) obtained from the ED of \(H^{2D}\). The velocity operator for light polarization along the tube axis is

\[
v_{2D}^{\sigma} = -\frac{i \hbar \pi}{\hbar} \sum_{\langle i,j\rangle, \sigma} \left( c_{i,\sigma}^{\dagger} c_{j,\sigma} - c_{i,\sigma}^{\dagger} c_{j,\sigma} \right) \delta_{\sigma,3}.
\]
Figure 3. Dependence on the correlation strength $U/t$ of one-photon (first bright state $E_{11}$ and second bright state $E_{22}$) and two-photon (TPA1, TPA2, TPA3, TPA4) transition energies for (4,0) (top panel) and (5,0) (bottom panel) zigzag $2n$-site clusters obtained from ED of the Hubbard Hamiltonian. The dotted lines used in part for TPA1 and TPA3 indicate their weak dipole strength at low correlation energies.

One finds that the velocity operator does not mix states with $\mu$ even and odd, as expected, and that the selection rule $\Delta \mu = 0$ is verified.

2. Results and discussion

ED has been performed for several values of the correlation coupling strength $U/t$, from the TB limit ($U = 0$), for which the zone-folding results were verified, to very large $U/t$. The parametric dependence of the Hamiltonian on the on-site Coulomb parameter allows a basic estimate of static screening-related effects in the excited-state spectra.

Energies of the first ($E_{11}$) and second ($E_{22}$) bright states are reported in figure 3. Notation $E_{ij}$ recalls the nomenclature used in TB calculations for optically active transitions from an $i$th van Hove singularity of the valence band to the $j$th singularity of the conduction band. The inclusion of the Coulomb interactions produces an evident blueshift of all the optical
transition energies with respect to those obtained in the TB limit. This is consistent with previous theoretical findings \[2, 3, 5\]. The present calculations find that the blueshift affects more consistently the $E_{11}$ transition energy and that a crossing between $E_{11}$ and $E_{22}$ occurs at about $U = 4t$, which can be considered as the bandwidth of a one-dimensional system. Moreover, the ratio between the two energies becomes smaller for increasing $U$. In figure 3, the energies of the two-photon absorption (TPA) states are also reported. One observes that states with a strong TPA activity are found above the first bright exciton for correlation energies $U/t \leq 3$. One weak TPA active state can also be found below the bright exciton, but it becomes important only for $U/t \geq 3–4$, where more than one state with a strong TPA activity is found below the first bright exciton. These results are found for both the (4,0) and the (5,0) nanotubes.

A calculated absorption spectrum is reported in figure 4 for an intermediate coupling regime, which is believed to describe better the real situation of SWNTs \[20, 35\].

One notes the stronger blueshift of the $E_{11}$ transition and the overall increase in the spectral intensity that can be related to the localization of the excitation. The difference between the behaviour of the first and second excitons can be understood looking into the wavefunctions. For the second exciton, there are significant contributions from states in which electrons in nearby sites have parallel spins, preventing the hopping of electrons among these sites and therefore depressing the importance of the correlation energy. A representative configuration, for example for the (4,0), is the following state $\langle \uparrow_1, \downarrow_2; (\uparrow_3, \downarrow_4); (\uparrow_5, \downarrow_6); (\uparrow_7, \downarrow_8) \rangle$, where sites from 1 to 8 can be empty or occupied by one electron with spin up (\uparrow) or spin down (\downarrow) or by two electrons. For the first exciton, the situation is different since the hopping of electrons is not frustrated by the spin arrangement and the contribution of the double occupied site becomes more important. In this case a representative configuration is $\langle \downarrow_1; (\uparrow_2, \downarrow_3); (\uparrow_4, \downarrow_5); (\uparrow_6, \downarrow_7); (\uparrow_8) \rangle$, where the above spin frustration is not found. This situation is relevant in the low and intermediate coupling regimes, because when the correlation energy becomes of the order of the bandwidth, the hopping among sites is in any case prevented and the first and second excitons behave similarly.
Figure 5. Bright and dark exciton states for the (4,0) and (5,0) nanotubes calculated with values of $t = 2.0$ eV and $U = 5.5$ eV [20].

The present calculations show that a manifold of dark states is always present below the bright states. TB calculations find only highly degenerate states for the first and second bright states. When the correlation energy is switched on, the degeneracy is broken also for values of $U/t$ less than 0.1 eV and the bright state is always the highest among this manifold of states. In our calculations, five states are calculated below the first bright one and, since two of them are doubly degenerate, a total of eight states (including the bright one) are obtained as expected considering also the electron spins. GW–BSE calculations predict only one dark state below the bright one. However, our result is similar to that found by Mazumdar et al [7], who calculated three states below the bright one. The result is also in agreement with Ando’s predictions that only one exciton state becomes bright when switching on the electron correlation and that this state is the higher one, among the four singlet excitons, for larger energy correlations [21]. Differences among these results are not clear at the moment, but they can be significant for the luminescence activity of carbon nanotubes. Different is the situation of the second exciton for which the degeneracy of states is again lifted, but the bright state is the intermediate state among this manifold for the (4, 0). This depends, however, also on the symmetry of the cluster since, for the (5,0), the second bright exciton is always the highest among the states of the manifold. The situation becomes more complicated when the ratio $U/t$ is of the order of 1 since, in this case, the dark states of the second exciton are also calculated below that of the first one. In any situation a number of dark exciton states are found below the first bright state. This result seems to agree with recent experimental measurements [16, 17], which show that more than one dark state is to be expected below the first bright one, although in the case of Harutyunyan et al, high-spin states are also considered. Our calculations show that the dark states are found at energies of the order of tens to hundreds of meV below the bright state. For example, in figure 5, we report the energy levels around the first bright exciton for the (4, 0) nanotube calculated with $t = 2.0$ eV and $U = 5.5$ eV, as suggested by Mazumdar et al [7] for real situations. One can see that the dark states below the bright state are found at 69, 98 and 260 meV. For the (5, 0) nanotube (see figure 5), we find the dark states at 119, 290 meV.

The value of $U$ is obtained as the difference between the on-site Coulomb parameter $U$ and the first nearest-neighbor Coulomb interaction parameter $V_1$ of the PPP Hamiltonian.
and 308 meV. These are values of the order of those found in experiments by Kiowski et al (40 and 110 meV) [16] and Harutyunyan et al (30–60 and 110–190 meV) [17].

The large energy gap between the bright state and the dark states suggests that a vibronic-like activation of the emission of nanotubes (the Herberg–Teller mechanism) is unlikely, as observed in short-chain carotenoids [22, 36], and it also excludes a repopulation of the bright state by thermalization. In this situation, emission occurs from the bright state in competition with internal conversion, as in longer-chain carotenoids [37].

Calculations of larger-diameter nanotubes are needed for a more quantitative comparison with experiments, but our results seem to suggest that more than one dark state is always expected below the first bright state and that their presence should be considered both for the optical and for the electronic properties of SWNTs.

3. Conclusions

In summary, we have presented full diagonalization results within the Hubbard model for the excitonic spectra of $\pi$ structures characteristic of SWNT. The calculations were possible using a small cluster approach that allows one to probe the van Hove singularities of the first Brillouin zone. The results allow one to obtain a qualitative view of the optical properties of the nanotubes in the intermediate and strong coupling regime. We found that in the strong coupling regime the two lowest bright states show a crossing and behave similarly. TPA states are found above the first bright states for small to intermediate correlation energies but below this state for larger correlation energies. Many dark states are calculated below the first bright one with energies that are of the order of tens to hundreds of meV, as recent experiments seem to suggest.

The approach allows simple extensions to include electron–phonon coupling [25, 26], which was found to be appropriately addressed with a molecular approach [38], and the presence of defects whose effects are very important for describing real cases.

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