Elucidation of the electronic structure of semiconducting single-walled carbon nanotubes by electroabsorption spectroscopy

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We report benchmark calculations of electroabsorption in semiconducting single-walled carbon nanotubes to provide motivation to experimentalists to perform electroabsorption measurement on these systems. We show that electroabsorption can detect continuum bands in different energy manifolds, even as other nonlinear absorption measurements have failed to detect them. Direct determination of the binding energies of excitons in higher manifolds thereby becomes possible. We also find that electroabsorption can provide evidence for Fano-type coupling between the second exciton and the lowest continuum band states.

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Semiconducting single-walled carbon nanotubes (SWCNTs) are being intensively investigated because of their unique properties and broad potential for applications \(^{1, 2}\). Recent theoretical investigations have emphasized the strong role of electron-electron interactions and the consequent excitonic energy spectra in SWCNTs \(^{3, 4, 5, 6, 7}\). While within one-electron theory two-photon absorption (TPA) begins at the same energy threshold as the lowest one-photon absorption, exciton theories predict a significant energy gap between the lowest two-photon exciton and the optical exciton \(^{8, 9}\). This energy gap gives the lower bound to the binding energy of the lowest exciton, and has been determined experimentally \(^{8, 9}\). Exciton theories predict a significant energy gap between the energy of \(E_x \) and the energy of \(E_{\text{1 manifold}} \) \(^{10, 11}\). Interference effects between \(E_x \) and the \(n = 1 \) manifold \(^{12}\), it has not been possible to determine its binding energy. TPA or transient absorption techniques used to determine the binding energy of the optical exciton in the \(n = 1 \) manifold \(^{12}\) are also difficult to verify directly. Clearly, measurements that can probe much broader energy regions of SWCNTs are called for.

In the present Letter, we propose electroabsorption (EA), which measures the difference between the absorption \(\alpha(\omega) \) with and without an external static electric field, as the ideal technique for understanding the overall energy spectra of SWCNTs. EA has provided valuable information on both conventional semiconductors \(^{13}\) and \(\pi\)-conjugated polymers \(^{14, 15, 16}\). The similarity in the energy spectra of \(\pi\)-conjugated polymers and SWCNTs \(^{7, 9}\) makes EA particularly attractive. EA spectroscopy of SWCNTs has already been attempted \(^{17}\), while continuous wave photomodulation spectroscopy has been interpreted as electroabsorption caused by local electric fields \(^{20}\). EA measurements are currently difficult as complete separation of semiconducting from metallic SWCNTs has not been possible to date. Recent advances in the syntheses of chirality enriched SWCNTs \(^{21}\) strongly suggest that EA measurements will become possible in select SWCNTs in the near future. We present here benchmark calculations of EA for several wide nanotubes that give new insights to their electronic structures, and provide the motivation for and guidance to experimental work.

As in our previous work \(^{7, 9}\), we choose the semipirical \(\pi\)-electron Pariser-Parr-Pople (PPP) model \(^{22}\) as our field-free Hamiltonian,

\[
H_0 = - \sum_{\langle ij \rangle, \sigma} t_{ij}(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_i^\dagger n_i + \frac{1}{2} \sum_{i \neq j} V_{ij}(n_i - 1)(n_j - 1).
\]

(1)

Here \(c_{i\sigma}^\dagger\) creates a \(\pi\)-electron with spin \(\sigma\) on the \(i\)th carbon atom, \(\langle ij \rangle\) implies nearest neighbors, \(n_i = c_{i\sigma}^\dagger c_{i\sigma}\) is the number of \(\pi\)-electrons on the atom \(i\), and \(n = \sum_{\sigma} n_{i\sigma}\) is the total number of \(\pi\)-electrons on the atom. The parameter \(t_{ij}\) is the one-electron hopping integral, \(U\) is the repulsion between two \(\pi\)-electrons occupying the same carbon atom, and \(V_{ij}\) the intersite Coulomb interaction. We have chosen Coulomb and hopping parameters as in our recent work \(^{7}\). In principle, we should also include the electron-phonon interactions.
not, however, describe the mixing of a quadratic in \( F \) linear or nonlinear absorption. excitons \([6, 7]\) in our discussion, as they play no role in \( n \) within the parallel to the nanotube axis and consider only the component of the static electric field along the same direction. The overall Hamiltonian is written as \[ H = H_0 + eFz = H_0 + \mu F, \] where \( e \) is the charge of the electron, \( F \) the field strength along the nanotube axis (taken to be the \( z \)-direction), and \( \mu \) the transition dipole operator along \( z \).

The EA is calculated in two steps \[17\]. We first diagonalize \( H_0 \) in the space of all single excitations from the Hartree-Fock ground state, using the single-configuration interaction (SCI) approximation \[16\]. Eigenstates of S-SWCNTs are of even \((A_g)\) or odd \((B_u)\) parity, and dipole matrix elements are nonzero only between states of opposite parity \[23\]. We calculate the field-free absorption spectra \( \alpha(\omega;0) \) from the calculated dipole matrix elements between the ground \( 1A_g \) state and excited \( B_u \) states \[2, 3\]. We now evaluate the matrix elements of \( \mu \) between all excited states of \( H_0 \), construct and diagonalize the total Hamiltonian \( H \) with the eigenstates of \( H_0 \) as the basis states, and calculate the new absorption \( \alpha(\omega;F) \). The EA is given by \[ \Delta \alpha(\omega;F) = \alpha(\omega;F) - \alpha(\omega;0). \]

The effect of the nonzero field is to mix \( A_g \) and \( B_u \) states. Within second order perturbation theory appropriate for weak fields, \( Ex1 \) undergoes a Stark energy shift \( \Delta E_{Ex1} \), given by

\[
\Delta E_{Ex1} = \sum_j \frac{|\langle E_1|\mu|jA_g\rangle|^2 F^2}{E_{Ex1} - E_{jA_g}},
\]

where the sum over \( A_g \) states includes the \( j = 1 \) ground state. In addition, \( A_g \) excitons that are forbidden for \( F = 0 \) become weakly allowed for \( F \neq 0 \). This transfer of oscillator strengths between \( A_g \) and \( B_u \) excitons is also quadratic in \( F \). Nondegenerate perturbation theory cannot, however, describe the mixing of \( A_g \) and \( B_u \) states belonging to continuum bands and the EA in these energy regions can be only calculated numerically. As we discuss below, the same is true for \( Ex2 \), which is buried within the \( n = 1 \) continuum. We have ignored the dark excitons \[6, 7\] in our discussion, as they play no role in linear or nonlinear absorption.

We first describe the \( n = 1 \) energy region separately. In Fig. 1(a) we have plotted the calculated linear absorption along with EA spectrum in the energy range corresponding to the \( n = 1 \) manifold for \( F = 10 \text{kV/cm} \) for the \((10,0)\) S-SWCNT. Figs. 1(b)–(d) show the EA spectrum for \( F = 50, 100, \text{and} 200 \text{kV/cm} \), respectively. EA for other S-SWCNTs, including chiral ones, are similar. The three most important features of the EA spectra are indicated in Fig. 1(a). The derivative like feature \( A \) corresponds to the redshift of \( Ex1 \). From Eq. (3), the redshift (as opposed to a blueshift) is the consequence of the existence of an \( A_g \) two-photon exciton that is closer in energy to \( Ex1 \) than the \( 1A_g \) ground state, and that also has a stronger dipole coupling to \( Ex1 \) \[17\]. In analogy to \( \pi \)-conjugated polymers \[17\], we have previously referred to the two-photon exciton state as the \( mA_g \) \[9\]. It is this state that is visible in TPA and transient absorption \[3, 8, 13, 14\]. Feature \( B \) in Fig. 1(a) corresponds to the field-induced absorption to the \( mA_g \). Feature \( C \) is a dip in the absorption due to the \( B_u \) state at the threshold of the \( n = 1 \) continuum band (hereafter the \( nB_u \) \[9\]). The continuum band is recognized by its oscillatory nature, and its appearance over a broad energy region where there is no linear absorption. EA can therefore give the binding energy of \( Ex1 \) directly, as the energy difference between the features \( C \) and \( A \).

The amplitude of the continuum band signal in Fig. 1 is much larger than that of the exciton at low field. This has been observed previously in a crystalline polydiacetylene \[10\]. Finite conjugation lengths prevent the observation of the continuum band EA signal in disordered noncrystalline \( \pi \)-conjugated polymers \[15\], but this signal will be observable in S-SWCNTs where the tubes are known to be long. Features due to the exciton and the continuum can be distinguished easily even when electron-phonon interactions lead to sidebands, from their different field dependence \[16\]. In Fig. 2(a) we show that the calculated field dependence of both the energy shift of \( Ex1 \) and the amplitude of EA signal due to \( Ex1 \) for \((6,5), (7,6), \) and \((10,0)\) S-SWCNTs are quadratic in \( F \) up to the largest...
nated. We calculated EA from the interference between two independent EAs. The very small EA signal due to the \( n = 1 \) states. Fig. 3(c) shows the superposition of these signals alone by removing all the coupling between them. The much larger signal in Fig. 3(b) is a consequence of the coupling between \( \text{Ex}2 \) and the \( n = 1 \) continuum states. We have further verified this by performing the Ea calculations with varying \( U / t \): larger Coulomb interactions imply larger Coulomb coupling between \( \text{Ex}2 \) and the \( n = 1 \) continuum, and give larger EA signal for \( \text{Ex}2 \). We have observed these characteristics in our calculated EA spectra for all S-SWCNTs.

Coulomb coupling between a discrete state with a continuum leads to the well-known Fano resonance, which manifests itself as a sharp asymmetric line in the linear absorption [24]. Calculation of the absorption spectrum of the \((8,0)\) S-SWCNT has previously found this coupling [3]. In contrast to this standard description of the Fano effect, the interference effect we observe in the EA spectrum is a consequence of transition dipole coupling between \( \text{Ex}2 \) and the \( n = 1 \) continuum states. One interesting consequence of this dipole coupling is that unlike \( \text{Ex}1 \), which undergoes redshift in all cases, \( \text{Ex}2 \) can be either redshifted [as observed in our calculations for \((6,4)\), \((7,6)\), and \((11,0)\) S-SWCNTs] or blueshifted [observed for \((6,2)\), \((8,0)\), and \((10,0)\) S-SWCNTs]. The reason for this is explained in Table I, where we have listed for the \((8,0)\) and the \((6,4)\) S-SWCNTs the dominant transition dipole couplings between \( \text{Ex}2 \) and \( A_g \) states along with the energy differences between them. Among these states, only one is from the \( n = 2 \) manifold, which is the \( mA_g \) state, the equivalent of the \( mA_g \) state in the \( n = 2 \) manifold. All other states belong to the \( n = 1 \) continuum. The relatively large energy difference between the \( mA_g \) and \( \text{Ex}2 \), comparable to that between the \( mA_g \) and \( \text{Ex}1 \), indicates that the energy shift of \( \text{Ex}2 \) is determined predominantly by the dipole-coupled \( n = 1 \) continuum states. States below and above \( \text{Ex}2 \) contribute to blue and red
TABLE I: Dominant transition dipole couplings between Ex2 and \( A_g \) states, as well as the corresponding energy differences. The \( m A_g \) state is labeled with an asterisk (*).

| \((n.m)\) | \(\langle Ex2|\mu|A_g\rangle/\langle Ex2|\mu|1A_g\rangle\) | \(E_{Ex2} - E_{1A_g}\) (eV) |
|---|---|---|
| \((8,0)\) | 8.31* | -0.423 |
| | 8.01 | 0.057 |
| | 6.22 | -0.103 |
| | 1.22 | 0.073 |
| \((6,4)\) | 15.3 | 0.049 |
| | 11.5 | -0.051 |
| | 11.1 | 0.081 |
| | 9.64 | -0.070 |
| | 9.45 | -0.080 |
| | 6.62 | -0.025 |
| | 6.45* | -0.402 |

shifts, respectively, and the energy differences in Table I rationalize blue (red) shift in the \((8,0)\) \((6,4)\) S-SWCNT. The magnitude of the energy shift of Ex2 in all cases is smaller than that of Ex1 because of partial cancelations, even as the amplitude of the EA signal of Ex2 is larger.

Correlated SCI eigenstates of the Hamiltonian (1) are superpositions of band-to-band excitations from the Hartree-Fock ground state. Furthermore, within the non-interacting tight-binding model as well as within Hartree-Fock theory, matrix elements of the component of the transition dipole moment along the nanotube axis are nonzero only for “symmetric” excitations, viz., from the highest valence band to the lowest conduction band, from the second highest valence band to the second lowest conduction band, etc. Hence the strong dipole couplings between Ex2 and proximate \( n = 1 \) continuum eigenstates of \( A_g \) symmetry necessarily implies that Ex2 eigenstate contains basis vector components belonging to both \( n = 1 \) and \( n = 2 \) manifolds. This is precisely the signature of Fano coupling. Table II shows the relative weights of the \( n = 1 \) one electron-one hole excitations in the correlated Ex2 eigenstates of several S-SWCNTs. These contributions are chirality-dependent, and reach as high as 30%.

The EA due to the \( n = 2 \) continuum in Fig. 3(b) is similar to that of the \( n = 1 \) continuum. The threshold of the \( n = 2 \) continuum is always detectable in our calculated EA spectra. Further confirmation of the band edge can come from measurements of its field-dependence, which is the same as for \( n = 1 \). Taken together with emission measurements that give the energy location of Ex2 [12], EA can then give the precise binding energy of Ex2.

In conclusion, we have performed benchmark calcula-

TABLE II: Relative weights of Hartree-Fock \( n = 1 \) excitations in the SCI Ex2 eigenstate of several S-SWCNTs.

| \((n,m)\) | \((8,0)\) | \((10,0)\) | \((6,2)\) | \((6,4)\) | \((6,5)\) | \((7,6)\) | \((9,2)\) |
|---|---|---|---|---|---|---|---|
| percentage | 3% | 2% | 23% | 12% | 20% | 33% | 26% |

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