Ideal dipole approximation fails to predict electronic coupling and energy transfer between semiconducting single-wall carbon nanotubes

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The electronic coupling values and approximate energy transfer rates between semiconductor single-wall carbon nanotubes are calculated using two different approximations, the point dipole approximation and the distributed transition monopole approximation, and the results are compared. It is shown that the point dipole approximation fails dramatically at tube separations typically found in nanotube bundles (~12–16 Å) and that the disagreement persists at large tube separations (>100 Å, over ten nanotube diameters). When used in Förster resonance energy transfer theory, the coupling between two point transition dipoles is found to overestimate energy transfer rates. It is concluded that the point dipole approximation is inappropriate for use with elongated systems such as carbon nanotubes and that methods which can account for the shape of the particle are more suitable. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3088846]

Single-wall carbon nanotubes (SWNTs) are highly conjugated carbon tubes that are a few nanometers in diameter and can be up to millimeters in length.[1] The excited electronic states of semiconductor-type SWNTs are quasi-one-dimensional excitons.[2] It is known that these spatially extended electronic excitations can migrate among SWNTs that are bundled together, thus quenching the fluorescence owing to the presence of metallic SWNTs.[3] Recent advances in purification and isolation have enabled studies of electronic energy transfer (EET) between SWNTs and molecular chromophores.[3,4] Here we examine the electronic coupling among SWNTs in order to understand EET involving SWNTs.

There are two main difficulties that need to be addressed when studying SWNT EET. The first is to obtain the electronic coupling matrix element that promotes EET. The most common method to calculate the electronic coupling between two molecules is the point dipole approximation (PDA) method, where the electronic coupling is described as the Coulombic interaction between transition dipole moments of D and A.[5] In this approximation, each molecule is represented by a single dipole located at the center of each molecule. It is known that the PDA method often fails at small separations in molecular systems.[6] Owing to the size of SWNTs compared to typical donor-acceptor separations, it is likely that the PDA method will fail. Even when using the PDA method, however, it is difficult to obtain the dipole strength of the transition because the radiative lifetime is obscured by thermal population of dark states in the exciton band.[7] The second difficulty is that there are a few closely spaced states associated with the lowest bright exciton transition (E_{11}) (Refs. 7–9) and each of these states might act as energy donors or acceptors.[10] Here we will focus on the first of these challenges: the evaluation of electronic couplings between SWNTs overcoming the limitations of the PDA method.

In the past decade, sophisticated quantum-mechanical approaches to this problem have been developed which range from the calculation of the actual interaction between quantum-mechanically derived transition densities[11,12] to more efficient but approximated strategies such as the distributed transition monopole approximation (TMA) method.[13,14] Each of these approaches is able to capture the shape of the transition density[15] throughout the donor and the acceptor molecules, which is the origin of the well-known breakdown of the PDA method at close separations in molecular systems.[16] Given the dimensions of the systems under study in this work, we adopt the TMA method to compute electronic couplings between SWNTs.

In the TMA method, the transition densities are described as a set of transition monopoles (charges) distributed among the atoms of the system. The Coulombic coupling between D and A is then given by

$$V_{\mathrm{TMA}} = \sum_{ij} \frac{q_{D,i}^{T} q_{A,j}^{T}}{R_{ij}}, \tag{1}$$

where q_i^T and q_j^T indicate transition charges located on sites i and j from D and A, respectively, and separated by a distance R_{ij}. Such charges are obtained by partitioning the transition density according to a Mulliken population analysis as is widely done for ground state charge distributions. In this work, excited states were calculated from time-dependent density functional theory, which has been shown to give the correct ordering of the SWNT excited states, i.e., the lowest excited state is dark with the bright states lying higher in energy.[9] Such calculations were carried out using the

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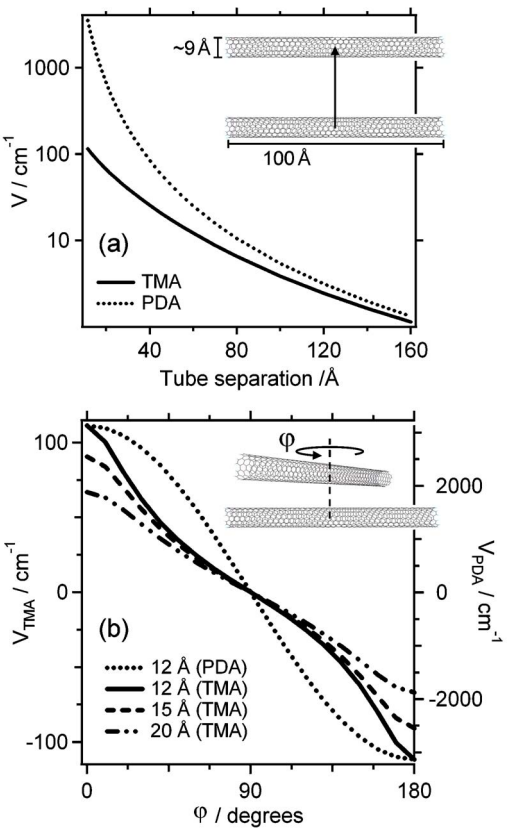

FIG. 1. (a) Electronic couplings predicted by the TMA and the PDA between two parallel (7, 5) SWNTs as a function of their center-to-center separation. (b) Electronic couplings for two (7, 5) SWNTs which are set center-to-center distance apart, as one tube rotates with respect to the other.

PBE1PBE hybrid exchange-correlation functional along with the STO-3G basis set. The use of a larger basis set has been demonstrated to shift excitation energies but not to change the qualitative picture of excited states.[9] In addition, very recent work has shown that EET couplings change typically less than 10% when enlarged basis sets are used, in contrast to more significant shifts obtained for excitation energies.[17] Due to the computational cost of the calculations, we consider SWNTs only 10 nm in length. This introduces quantum confinement, giving rise to discrete energy levels rather than a band. Consideration of finite SWNTs can still be realistic because the exciton can be localized due to defects, interactions with the local dielectric environment, average tube length, intertube interactions, and exciton-phonon coupling. Using the PBE1PBE/STO-3G method outlined, we report the Coulombic coupling values between the bright states in pairs of (7, 5) and (7, 6) SWNTs, which have tube radii of ~9 Å, calculated using both the TMA and PDA methods, and show that the PDA method fails even at large tube separations.

Calculated Coulombic coupling values are shown in Fig. 1. In the top panel, two (7, 5) SWNTs are positioned parallel to each other, and the Coulombic coupling was calculated at various separation distances using both the TMA and PDA methods. Very similar results were found for pairs of (7, 6) SWNTs and for one (7, 5) and one (7, 6) SWNT together. In bundles, the SWNTs are side by side in van der Waals contact with a center-to-center tube separation of ~12–16 Å with ~2.5 Å between tube surfaces.[18] Our calculations indicate that in this regime of separation values, the PDA method overestimates the Coulombic coupling by an order of magnitude compared to the TMA method. In fact, the PDA method fails at remarkably large SWNT separation values, even >100 Å, which corresponds to over ten tube diameters.

The lower panel shows calculated Columbic coupling values for a pair of SWNTs a set distance apart with one tube rotated with respect to the other through a half rotation. The electronic couplings are calculated using both the PDA and TMA methods with a tube separation of 12 Å. The PDA method overestimates the coupling by more than an order of magnitude (compare the two vertical axes). As well, the relationship between coupling and the angle between SWNTs is predicted to be simply sinusoidal, while the TMA method reveals a slightly more complex relationship, where the coupling drops more rapidly when the SWNTs are not perfectly parallel. Also, these calculations confirm that energy transfer should be most efficient when two SWNTs are parallel to each other, as the V^2 term will be the largest.

These results lead us to conclude that the PDA method is inadequate for SWNTs, owing to their large size and distinctly nonspherical shape. The PDA effectively concentrates the transition dipole strength, which is spread over the length of the SWNT, into one point. When two tubes are placed side by side, the distance between the two point dipoles is the minimum center-to-center distance between the two tubes. In the TMA method, the transition dipole strength is spread over the length of the SWNT, and the interaction between a monopole on one tube with a monopole of the other depends on the position of the monopole along the tube. The separation between monopoles at the same position on both tubes will be the center-to-center tube separation, but otherwise the separation can be much larger. Thus, the TMA method accounts for the shape of the SWNT, while the PDA method, which does not account for the shape, grossly overestimates the coupling values.

The failure of the PDA method can also be considered from the perspective of dependence on tube length (L). In the case of a completely delocalized exciton in a long tube, the transition dipole moment (μ) scales with tube length as $\mu \propto \sqrt{L}$, and thus the oscillator strength (f) scales as $f \propto \mu^2 \propto L$. Using the PDA method, the coupling (V_{PDA}) between two parallel tubes is also proportional to tube length $V_{\mathrm{PDA}} \propto \mu^2 \propto L$. However, a different result is found using the TMA method, where the interactions between small pieces of transition dipole are considered. Each piece contributes a transition dipole strength of $\mu_i \propto \sqrt{L}/L \propto L^{-1/2}$, and so the interaction between two pieces is $V \propto \mu_i \mu_j \propto 1/L$. By summing the interactions along the tube, we obtain $V_{\mathrm{TMA}} \propto LV \propto 1$. Thus, while the PDA approach implies that there is a linear dependence of the coupling strength on the tube length, the TMA method finds that the coupling strength is independent of tube length.

An accurate calculation of the Coulombic coupling is of great importance to calculations of EET. In Förster resonance energy transfer (FRET) theory, the expression for the rate of energy transfer (k) depends on the square of the coupling

$$k_{ij} = \frac{2\pi}{\hbar}|V_{ij}|^2 J_{ij}. \quad (2)$$

Here, J_{ij} is the spectral overlap between donor state i and acceptor state j. This is found by computing the overlap integral between the fluorescence spectrum of the donor state and the absorption spectrum of the acceptor state. These spectra can be measured or they can be simulated using a calculated line shape function.[6,19] Here we have calculated line shape functions based on four discrete oscillators of frequency 17, 117, and 1500 cm^{-1} and the SWNT type-dependent radial breathing mode, together with a single overdamped Brownian oscillator with a reorganization energy of 50 cm^{-1} and a modulation frequency of 1000 cm^{-1}.[9,19] The amount of inhomogeneous broadening depends on the individual sample, so a representative value for disorder was used, $\sigma = 80\ cm^{-1}$. It is known that the lowest energy state of each SWNT is dark and that the lowest energy bright state is ~100 meV above the dark state.[7–9] The spectral overlaps of the bright states for two (7, 5) tubes and two (7, 6) tubes were calculated using the parameters above and found to be 7.07 and 7.30 eV^{-1}, respectively. Using these values and the calculated Coulombic couplings, the rate of energy transfer between two (7, 5) tubes with a 14 Å separation is predicted by the PDA method to be $4.0 \times 10^{15}\ s^{-1}$ while the TMA method calculates a rate of $9.7 \times 10^{12}\ s^{-1}$. This latter result, an energy transfer time of 100 fs, indicates that energy transfer among SWNTs in a bundle can be very rapid and certainly able to compete with the short excited state lifetime of SWNTs.

This calculation oversimplifies the problem: a weakly allowed state is thought to exist between the dark and bright states and it might influence the energy transfer dynamics. For example, we calculate the spectral overlap between the bright state of a donor SWNT and the weakly allowed state of an acceptor tube to be 9.47 and 9.51 eV^{-1} for pairs of (7, 5) and (7, 6) tubes, respectively, larger than the spectral overlap of two bright states. However, the Coulombic coupling between bright and weak states is smaller than the coupling between two bright states. For example, for two (7, 6) SWNTs 14 Å apart, the bright-bright coupling calculated using the TMA method is 97 cm^{-1} and the bright-weak coupling is 65 cm^{-1}. This compensates for the increase in spectral overlap and the resulting energy transfer rate from a bright donor state to a weakly allowed acceptor state ($5.9 \times 10^{12}\ s^{-1}$) is lower than the bright-bright rate ($1.0 \times 10^{13}\ s^{-1}$). The two rates are comparable, suggesting that exciton population in the weakly allowed state must be considered in calculations of the overall energy transfer from one SWNT to another. The population kinetics within these states must then be considered in order to calculate an accurate value of the energy transfer rate. As well, it has been shown that larger basis sets may be required for the calculation of smaller electronic coupling values such as those for forbidden transitions.[20] While the STO-3G basis set is adequate for the calculation of the bright-bright coupling, a larger basis set may be required for bright-weak or bright-dark coupling. This point is in fact supported by previous calculations in which only small variations in the oscillator strength of the bright states were found when the basis set was enlarged from STO-3G to 6-31G.[9]

Along with these complications, both of the methods for calculating Coulombic coupling values presented in this work are approximations; a transition density cube calculation might obtain more accurate values but perhaps a larger basis set would be a primary consideration.[11] The TMA method has been shown to predict exciton splittings consistent with supermolecule calculations in conjugated polyene chains, where the PDA approximation leads to considerably large errors.[21] We are thus confident that our main conclusion is essentially correct, i.e., that the PDA method tends to overestimate the rate of energy transfer between SWNTs by several orders of magnitude.

The observation that multipole expansions do not accurately describe nonspherical molecules dates back to London's work[22] in the 1940s. In his discussion of ground state interaction energies he notes that for long oscillators in chain molecules, the use of point multipoles located at the center of each molecule misrepresents the situation. The interaction of another molecule with this long chain molecule would depend on the relative position of the molecules. Thus, London proposed that the molecule be represented by several monopoles located along the molecule to take into account the extent of the oscillator.

More recently, the breakdown of the PDA method has been observed in coupling calculations of other large nonspherical particles. Schrier and Wang[23] showed a similar trend for semiconductor nanorods. In their study, PDA values were found to deviate from Coulombic couplings estimated from quantum-mechanically derived transition densities by a factor of 2–3.[11] The much stronger deviation found for SWNTs is likely due to the smaller aspect ratio of the CdSe nanorods (~3) relative to the aspect ratio of the SWNTs studied in the present work (~10). A study by Beljonne *et al.*[21] of interchain interactions in conjugated materials compared exciton coupling energies between polyene chains calculated using the PDA method and using multicentered monopoles. This work also found that the PDA approach tended to overestimate the coupling between long chains. A further study by Beljonne *et al.*[13] of energy transfer in rigid, linear, acceptor-capped conjugated polymers found that the PDA method failed to account for local interactions between different parts of the polymers. This resulted in the conclusion that the PDA method was inadequate for the prediction of coupling values, particularly with respect to the rotational orientation of the donor and acceptor molecules. The general conclusion of the PDA method's inadequacy for nonspherical particles was again evidenced in the work of Wong *et al.*,[24] which evaluated the electronic coupling between a six unit linear oligomer and a porphyrin with a planar structure. Again, the PDA method was found to overestimate the electronic coupling at small separations by more than an order of magnitude. Thus, our results agree with these findings and confirm for the case of SWNTs the paradigm that the PDA should be completely avoided in the study of EET in elongated systems.

In summary, the PDA method has been shown to fail for calculations of Coulombic coupling in (7, 5) and (7, 6)

SWNTs even at large tube separations. At tube separations typically found in SWNT bundles, the PDA method overestimates the Coulombic coupling by an order of magnitude relative to calculations performed using the TMA method. While both of these methods are approximations, our calculations qualitatively show that the highly elongated shape of the tubes causes the PDA method to overestimate the magnitude of the coupling. Our results extend to SWNTs the paradigm that the PDA method strongly fails to describe electronic energy migration in extended nanoscale systems. The PDA method is often used to calculate electronic coupling values for use in FRET theory with the ultimate purpose of determining molecular separations or energy transfer rates. In this work, we have shown that at tube separations typically found in SWNT bundles, the PDA method overestimates the energy transfer rate relative to that predicted by the TMA method by more than two orders of magnitude. As the use of FRET becomes more commonplace, it is important to highlight the possible pitfalls of using single-center multipole approximations and appreciate that the technique used to evaluate electronic coupling must be chosen and employed judiciously.

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