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Exploring Two Approximate Coupling Models in Exciton Transport

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ABSTRACT Point dipole and line dipole coupling approximations are two methods for approximating the transition dipole coupling between two conjugated organic molecules. Transition dipole couplings are an important factor in determining energy transfer between two non-covalently-bonded molecules. Transition dipole couplings were mathematically calculated by two methods, applying the point dipole and line dipole approximations. The calculations were implemented using Octave, an open source computer programming language. Using this tool, software was created to efficiently analyze the differences between transition dipoles calculated using the two methods, for a variety of relative orientations of two model conjugated organic molecules. Custom-built software was created to model two polymers with varying relative orientation within three-dimensional space. As illustrative examples, we analyzed the results of polymers that were parallel, and at a forty-five degree tilt. We also analyzed the dependence of the coupling of two parallel polymers on a key parameter of the line-dipole model, the number of sub-units over which the transition was distributed. We compare the point dipole and line dipole couplings, finding that the line-dipole coupling method generally produces smaller couplings.

INTRODUCTION

Electronic coupling, also called transition dipole coupling, governs through-space energy transfer between two molecules. When this energy transfer occurs, the electrons in a donor molecule relax from an excited state into their ground state, while the electrons in an acceptor molecule simultaneously transition from their ground state into an excited state. Here we implement two mathematical methods for calculating the transition dipole couplings between two polymer

chromophores (Beenken and Pullertis, 2004). Chromophores are regions within an organic molecule that can experience electron excitation when exposed to light. These chromophores are located on large conjugated polymers, which are macromolecules. This type of polymer is a multi subunit molecule with a chain of alternating single and double bonds, which allow for the movement of electrons throughout the molecule. Polymer chains consist of many chromophores,

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generally locally-planar regions within the polymer chain that are interrupted by twists and kinks. In this work, we use small planar model chromophores rather than attempting to model an actual polymer chain. This strategy substantially reduces computation cost and complexity, while still allowing us to consider the key molecular properties that affect transition dipole coupling.

The point dipole method models each chromophore as a single point in space, hosting a single transition dipole vector. This approximation is valid when the intermolecular distance is much greater than the size of the molecules themselves (Kaibo et al., 2014). In contrast, the line dipole method distributes the transition dipole vectors associated with each molecule through space in a manner consistent with the shape of the molecule. This method is more accurate than the point dipole method when intermolecular distances decrease to lengths relative to the size of the defined molecule. Our modelling strategy excludes Dexter coupling, an exchange-mediated coupling mechanism that becomes important at distances of less than 1 nm. (Scholes 2004).

To calculate a transition dipole using the point dipole approximation, each chromophore is assigned a single-point position in three dimensional space (\mathbf{R}) (Riplinger et al., 2009). A transition dipole vector ($\boldsymbol{\mu}$) is also assigned to each chromophore. This approximation does not take into account the shape or physical size of the chromophores, but does model their relative position, orientation, and transition dipole strength (Scholes, 2004). Neglecting the size of the chromophore is a good approximation at large intermolecular distances, but breaks down as the distance between molecules becomes comparable to the size of the molecules themselves. Coupling between two chromophores at positions \mathbf{R}_1 and \mathbf{R}_2 , with transition dipole vectors $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, is calculated as defined below in equation 1 (Beenken & Pullertis, 2004).

$$V_{12} = \frac{1}{4\pi \epsilon_0} \left(\frac{\boldsymbol{\mu}_1 \boldsymbol{\mu}_2}{|\mathbf{R}_{21}|^3} - 3 \frac{((\boldsymbol{\mu}_1 \mathbf{R}_{21})(\boldsymbol{\mu}_2 \mathbf{R}_{21}))}{|\mathbf{R}_{21}|^5} \right) \quad (1)$$

The point dipole coupling is V_{12} , and \mathbf{R}_{21} is the vector connecting the position of the two

chromophores (Beenken & Pullertis, 2004).

In contrast, the line dipole couplings are calculated mathematically according to equation 2 (Beenken & Pullertis, 2004).

$$V_{iA} \sim \sum_{a=1}^{L_A} \sum_{d=1}^{L_D} \psi_{iA}(a) \left(\frac{\boldsymbol{\mu}_1 \boldsymbol{\mu}_2}{|\mathbf{R}_{21}|^3} - 3 \frac{((\boldsymbol{\mu}_1 \mathbf{R}_{21})(\boldsymbol{\mu}_2 \mathbf{R}_{21}))}{|\mathbf{R}_{21}|^5} \right) \cdot \psi_{jD}(d) \quad (2)$$

In the line dipole method, each model chromophore is broken into a number of subunits. The line dipole coupling is a measurement of the sum of interactions between all subunits of the donor chromophore and all subunits of the acceptor chromophore. \mathbf{R}_{21} in equation 2 is the vector connecting the centers of the two subunits. The variables $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are the transition dipole vectors of the subunits. In addition, ψ is a discrete wave function required by the implementation of subunits. The wave function is used in order to describe the location probability of electrons within a molecule. This implication of the ψ component can be calculated mathematically as (Beenken & Pullertis, 2004).

$$\psi_{iA}(a) = \frac{\sin(k_{iA} a)}{\sum_a \sin(k_{iA} a)} \quad (3)$$

Where α is the number of subunits within the molecule. K is a constant of pi divided by the length of the polymer (L_A) plus one. This equation is displayed below (Beenken & Pullertis).

$$k_{iA} = \frac{\pi}{L_A + 1} \quad (4)$$

The dependence of the transition dipole couplings calculated using both methods on the relative orientation of the chromophores was explored. These methods include testing the effect of distance on the interaction between these chromophores, which was performed whilst simultaneously exploring orientation in terms of angle of tilt, such as parallel orientation and tilt of forty-five degrees.

METHOD

All calculations described in this work were carried out using custom built software created using the Octave programming language and environment. To construct computer models of

two chromophores in three-dimensional space, first the two chromophores were each assigned a center position in x , y , z space and an orientation vector. One chromophore was assigned to be the donor, and the other was designated the acceptor. For the purpose of calculating the line dipole coupling, each chromophore was also designated to contain a number of subunits. This factor was used to implement the distribution of transition dipole vectors throughout the span of the polymer.

To control the relative orientation of the chromophores, chromophore coordinates and orientation vectors were transformed into spherical polar coordinates. The components of spherical units are best illustrated given Figure 1 below:

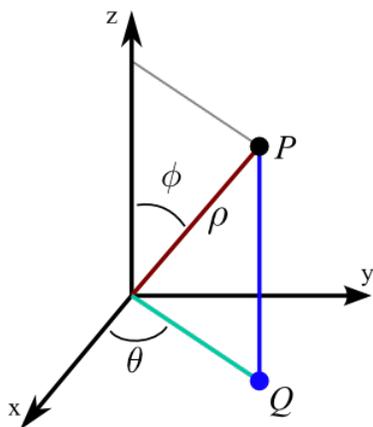


Figure 1. Spherical coordinates are demonstrated on a three dimensional axis. Where P represents the coordinate in three-dimensional space.

The ϕ component acted as the tilt within three dimensions, and was defined from the range of zero to one hundred and eighty degrees. The θ component was the rotation aspect, and could be defined in a range of zero to three hundred and sixty degrees. Using this system, the orientation vectors for the two chromophores were manipulated to control the dihedral angle between the two transition dipole vectors. The interchromophore spacing R_{12} could also be manipulated.

The model polymer chromophores considered here are not intended to accurately represent any specific polymer. The parameters considered are

loosely based on experimental measurements of poly-3-hexylthiophene from literature. Though polymer chains contain multiple chromophores with varying spatial configuration within their chains, we modeled only a pair of planar chromophores. This model acts as the simplest manner to picture the interaction of two chromophores within three dimensional space, and displays the potential to apply these computational tools to any number of polymers.

Point-dipole and line-dipole couplings were calculated according to equations 1 and equation 2, respectively. To study the relationship between these two methods, we calculated couplings as a function of interchromophore distance for two relative orientations of the chromophores. We also investigated the dependence of the magnitude of the coupling at close interchromophore spacing on the number of subunits used to calculate the line dipole.

RESULTS AND DISCUSSION

Figure 2 shows coupling calculated by both methods for two chromophores with parallel orientation as function of the interchromophore distance R_{12} . The transition dipole moment of the chromophores was chosen to be 15 Debye. For the line dipole calculation each chromophore was designated to contain ten subunits, within a total size of 10 nm. The transition dipole of a polymer chromophore generally depends on its length, as well as other properties. The chosen 15 D value is a reasonable estimate of the transition dipole of a 10 nm long chromophore in a conjugated polymer. The geometry of the chromophore was defined as linear for both the acceptor and donor. At the shortest distance employed, 0.2 nm, the point dipole coupling is almost a factor of ten larger than the line dipole coupling. This distance is similar to the closest interchromophore distances experimentally measured in solid state conjugated polymers. As the interchromophore distance increases, both couplings decrease. At large separation the couplings both asymptotically approach zero, as expected.

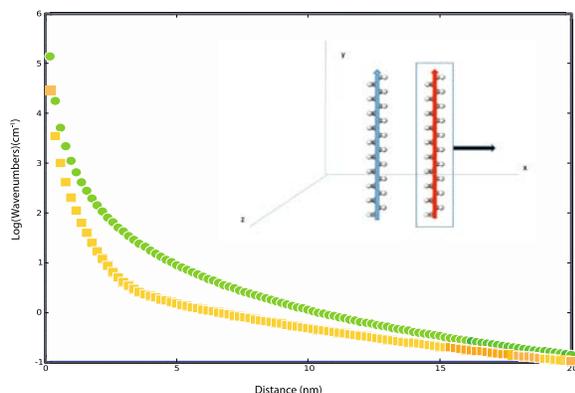


Figure 2: Line Dipole (yellow) and point dipole (green) electron coupling calculated over distances of 0.2 to 20.0 nm. The calculated electronic coupling value was measured in wavenumbers (cm^{-1}). The two model chromophores are arranged in a parallel relative orientation. In the top right hand corner demonstrates the relative spatial arrangement of the donor (blue) and acceptor (red) chromophores.

Figure 3 shows the results of a similar test in which one chromophore has been tilted by $\phi = 45^\circ$. Again 15 Debye transition dipoles were employed, with ten subunits designated for each chromophore in the line-dipole calculations, and a linear geometry for both the acceptor and the donor. At the smallest interchromophore spacing, again 0.2 nm, the point dipole coupling was again about ten times larger than the line dipole coupling. As the interchromophore distance increased, the couplings again converged towards the expected asymptote of zero coupling.

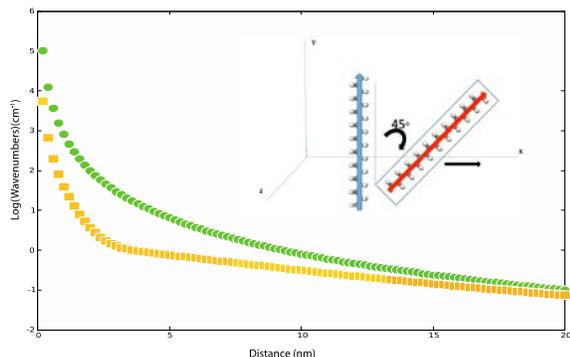
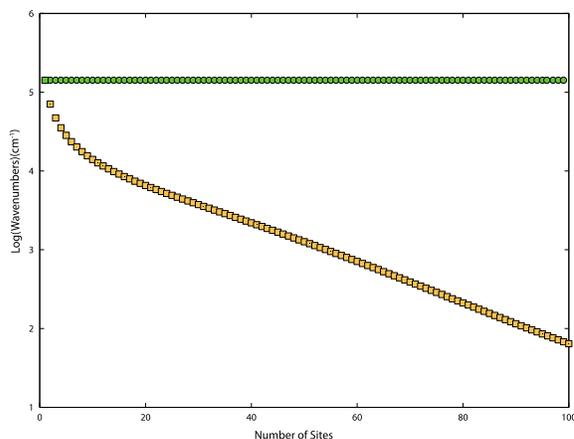


Figure 3: Line dipole (yellow) and point dipole (green) electronic coupling calculated value over distances of 0.2 to 20.0 nm. The calculated electron coupling was measured in wavenumbers (cm^{-1}). There is a $\phi = 45^\circ$ tilt in the relative orientation of the two chromophores.

Figure 4 shows couplings calculated as a function of the number of subunits employed for the line dipole calculation. Again 15 Debye transition dipoles were employed, and the chromophores adopted the same parallel conformation used in the calculations shown in Figure 2. Note that the length of the chromophore remains constant at 10 nm as the number of subunits varies. As the number of subunits increases, the length of each subunit correspondingly decreases. Therefore the transition dipole moments remain the same regardless of chain length. The interchromophore spacing was 0.2 nm, within the range where the point dipole approximation is expected to fail. Dexter coupling may also be important in this regime, and that mechanism is excluded from our model. The number of subunits was altered in both chromophores simultaneously. As the number of subunits increases, we observe that the line-dipole coupling diverges from the point dipole result, yielding much smaller couplings. The calculated couplings decrease by more than three orders of magnitude as the number of sites varies from one to one hundred. Our expectation was that the line-dipole calculation would converge upon an asymptotic value as the number of subunits increased, but this behavior was not observed in the range displayed in Figure 4.

Figure 4: Line Dipole (yellow) and point dipole



(green) electron coupling at a distance of 0.2 nm, and a parallel orientation.

The same configuration was tested on a range of number sites, as displayed in Figure 5. The interchromophore spacing was altered to 2.0 nm, and again the total length of the chromophores is fixed at 10 nm. In this regime the effects of

Dexter coupling can be safely neglected. As the number of subunits increases in the acceptor and donor models, the line dipole values again diverge from the point dipole values. Line dipole values decreased by more than one and a half orders of magnitude as the number sites increased from one to one hundred. In this case we observe the asymptotic behavior expected as the number of subunits increases. The asymptotic value is achieved by around 20 subunits, or one subunit per 0.5 nm of chromophore length.

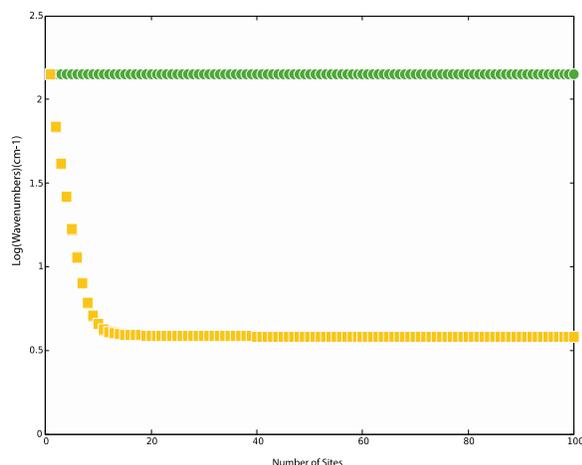


Figure 5: Line Dipole (yellow) and point dipole (green) electron coupling of 2.0 nm, and parallel orientation.

CONCLUSION

Large differences between the line dipole and point dipole methods were observed as interchromophore distance, relative orientation, and the number of subunits employed in the line-dipole calculation were varied. The line-dipole method is expected to be a more accurate method for calculating electronic coupling between two chromophores at shorter distances, due to the breakdown of the point-dipole approximation and the interchromophore distance becomes smaller than the chromophores themselves. As seen in figure 2, the point-dipole electronic coupling is over an order of magnitude greater than line-dipole coupling in this size regime. At close distances of 0.2 nm the point dipole and line dipole coupling values were 1.42×10^5 (cm^{-1}) and 2.83×10^4 (cm^{-1}), respectively. This data denoted a large difference in values in coupling methods at close distance.

Figure 3 shows that this difference persists when the relative orientation of the two chromophores changes. At large distances both methods show convergent. At small distances the line dipole method yields couplings up to an order of magnitude smaller than the point dipole. Interestingly, comparison of figure 2 and figure 3 reveals slightly different dependence of couplings on interchromophore distance, depending on the relative angle between the two chromophores. It is not yet clear why this occurs.

The convergent behavior by both coupling methods is achieved by a distance of approximately 20 nm. This demonstrates that the point dipole method can be considered accurate in the size regime above 20 nm.

Figure 4 shows how the calculated electronic couplings depend on the number of subunits employed in the line dipole calculation, for two closely spaced, parallel chromophores. The point dipole model does not employ subunits, so the calculated coupling via this method remains constant. Line dipole couplings were observed to decrease as a function of the number of subunits employed, without approaching an asymptote. Figure 5 analyzed the same dependence of coupling on number of subunits, but employed a larger interchromophore distance of 2.0 nm. This test showed a lesser disagreement between line and point dipole values, and the calculated couplings approach an asymptote as the number of subunits increases.

Through calculations performed using custom-built software, we have explored the regime wherein the point dipole-coupling model fails to accurately calculate the total electronic coupling between two conjugated polymer chromophores. Ultimately, we showed that the point dipole model results in larger coupling values at all relative chromophore orientations modeled. Line dipole couplings were generally an order of magnitude or more smaller at interchromophore distances similar to chromophore size, with the two methods converging at larger distances. The line dipole method was observed to converge upon asymptotic values as the number of subunits employed increased for larger interchromophore spacings, but not at smaller distances.

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