EXCITON DYNAMICS

# Simplifying organic complexity

Predicting the properties of complex organic molecules from first principles is computationally restrictive. But by modelling their behaviour as that of a series of scattering vertices, accurate calculations of their electronic structure become possible.

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Over the past several years, the field of molecular electronics has developed rapidly from conception to working semiconductor devices. In such devices, the semiconducting medium is typically composed of π-conjugated organic polymer building blocks in which the electronic properties of the device are inherently related to the electronic states of the individual molecules. The electronic properties can be tuned by chemical modification of the polymer and its side chains. From a theoretical standpoint, the description of molecular excited states remains a formidable challenge, even for modest sized systems in spite of the advance of more efficient algorithms and the exponential increase of computational power. On page 631 of this issue, Wu and colleagues[1] address the challenge of predicting the excited-state properties of molecular electronic material by breaking down a large π-conjugated organic system into a series of simpler linear excitonic segments, connected together at vertices that define the boundary conditions and interactions of each element appropriately. In doing so they build a surprisingly accurate but computationally tractable description of the excited states based upon the geometry and connectivity of the original molecule. This connection between the molecule's geometric connectivity and its excitonic states provides a potentially powerful avenue for substantially increasing the speed of accurate quantum chemical and time-dependent density functional theory calculations of such states.

It has long been recognized that the excitonic states of organic π-conjugated systems can be reasonably approximated within a non-interacting model[2]. If we take the conjugated states for an organic polyene chain with $N$ repeating units to be linear-combinations of $p_z$-orbitals localized on each of the carbon atoms along the chain, then within a non-interacting approximation, we can approximate the optical gap between the highest occupied and lowest unoccupied states as $\Delta E = E_{N/2+1} - E_{N/2} \propto 1/N$ when $N$ is taken to be large. Because the persistence length of a π-conjugated domain is often smaller than the actual length of the conjugated polymer owing to defects that localize the π electrons, one can relate the optical gap to the average persistence length of the π-conjugated system. For typical conjugated polymers, this length is of the order of 10 to 15 repeating monomeric units depending upon the system and how the sample was prepared. Strictly speaking, molecular excitonic states involve at least two quasi-particles — an electron promoted to an unoccupied orbital and a hole remaining in a formerly occupied orbital. If we represent this two-particle state in terms of the relative and centre-of-mass motion of the electron–hole pair, we can effectively adopt a 'single' particle description in which the centre-of-mass motion is approximately decoupled from the relative motion of the Coulomb-bound electron–hole pair.

The difficulty begins when one wishes to extend this notion to systems with multiply connected segments, such as a dendrimer molecule. Such systems are of current interest because of their ability to act as 'energy funnels' in light-harvesting applications such as solar cells and photovoltaic devices. As in linear polymers, one can think of a dendrimer as a collection of one-dimensional domains linked at vertices that may connect multiple domains. The quantum wave functions from each of the connected domains must satisfy scattering boundary conditions at the vertex as determined by the specific chemical nature of the intersection. Hence, the excitonic states of a multiply connected dendrimer are directly related to the connectivity map

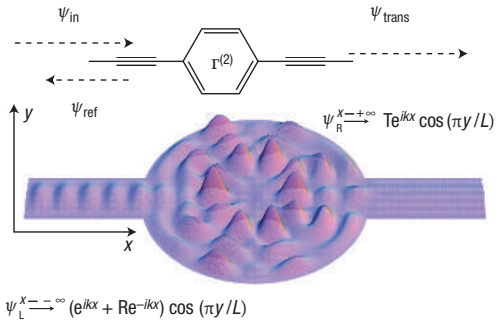


**Figure 1** Treating each part of a large conjugated molecule in terms of scattering vertices (top) within it makes calculation of excited states throughout the whole computationally tractable. Much as nodal patterns within the circular cavity (bottom) determine the reflection and transmission properties of an electromagnetic waveguide, the chemical nature and bonding arrangement determine the properties of the junctions.



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of the molecule itself. In such, the excitonic states of a multiply connected molecule can be reduced to the eigenmodes of a classical wave guide. This analogy is depicted in Fig. 1, where the two-input junction is represented by a circular cavity with linkages to the left and right. The scattering wave solutions are the eigenfunctions of the Helmholz equation in two dimensions with homogeneous Dirichlet boundary conditions[3,4]. Here the wave function scatters in from the left, undergoes constructive and destructive interference within the junction, and is transmitted and reflected to the right and left respectively. The nodal pattern within the junction depends on the energy of the incident wave and the specific details of the junction. All this internal information is encoded in the scattering matrix for the particular junction, which in turn determines the transmission and reflection coefficients for the scattering wave. Thus, just as transmission through a waveguide can be computed by connecting the scattering matrices of the individual junctions, the exciton propagation can be approximated through a molecular waveguide by combining the appropriate scattering matrices for each vertex in sequence.

The transmission and reflection amplitudes in the waveguide depend upon both the geometry of the cavity and the momentum (hence energy) of the incident wave. Consequently, the scattering matrices depend upon the chemical nature of the junction and the momentum (and energy) of the exciton. Either heuristic arguments or more precise determinations (via time-dependent density functional theory calculations, for example) can be used to compute a library of scattering matrices and thereby generate a 'toolbox' of junctions to approximate the excitonic states of very large multiply connected dendrimer systems. The accuracy of this approach can be readily checked by performing *ab initio* calculations on systems with a small number of vertices connected by short segments. Indeed, as Wu *et al.*[1] show, the simple exciton scattering model does a remarkably good job at predicting energies and properties such as oscillator strengths, even compared with the best available approaches for excited states.

Quasi-one-dimensional systems continue to yield theoretical surprises, which often are of academic interest but have little immediate practical benefit. In the present case, however, given the increasingly urgent need to find alternative means of energy generation and the consequent push to develop novel light-harvesting materials based on organic conjugated polymer materials, the exciton scattering model could soon be put to good use in the design and development of new organic materials.

## REFERENCES

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