

Patrick Fowler
Graphs and graph representations in chemistry & molecular physics

1 Individual Project's contribution to the CRP

1.1 Aims and Objectives

In the context of the project, this AP is interested in graph theory as a tool for modelling geometries, energies and properties of chemical systems.

Representations: In chemistry, molecules have many levels of representation, from a conventional flat chemical formula, to ball and stick stereo-models, from graphs, embodying only connectivity, to 3D contour maps of densities derived from single-particle or many-body wave functions, showing electrical properties key to intermolecular interactions. Different levels of chemical information are encoded in, and can be extracted from, molecular representations, imposing different requirements in their construction. A drawing that is to convey useful stereochemical information should be faithful to realistic relative bond lengths and angles. Given the high-throughput nature of the modern pharmaceutical drug-discovery process, such representations must be derived in a simple and efficient way from the molecular graph alone.

Chemical Graphs: Chemical graphs are connected, and of specified maximum degree. Usually the maximum degree is ≤ 3 , representing the possible coordination numbers in an unsaturated hydrocarbon or similar system. For structural applications such as isomer counting for general organic compounds, this is raised to ≤ 4 , and so on. Chemical graphs often display considerable symmetry; they are often bipartite, and many belong to special graph classes (fullerenes, benzenoids, chemical trees (polyenes), cycles (arenes), circulenes, radialenes), some characterisable as graph products, or as results of uniform operations on graphs.

Geometric representations: Approaches to geometry generation based on adjacency (in effect Laplacian) eigenvectors have been successful in picturing fullerenes (cubic polyhedra with face sizes 5 and 6 only). Catalogues of such maps feature heavily in the Atlas of Fullerenes [1], and are especially useful for systematic derivation of molecular signatures in infrared, microwave and nuclear magnetic resonance spectroscopies. They also allow deduction directly from the graph of crucial properties such as non-zero dipole and higher multipole moments, chirality. Recent work by Estrada [2] suggests that Laplacian eigenvectors can also be used to determine vibrational amplitudes and energies in a graph- theoretical version of the molecular force field.

Electronic structure: The adjacency eigenvectors play a key role in qualitative theories of molecular electronic structure, where they correspond to, for example, the π orbitals of conjugated carbon systems. There is a long history of research on 'chemical graph theory', but there is still great potential for a closer union between mathematics and applications, with emphasis on generic classificatory work. Graph-alone theories cannot be expected to recover the minutiae of the chemistry, but can give clues to broad structure-property-reactivity relationships that influence molecular stability, electronic configuration, and types of reactivity. The fullerene area is one where this approach has been very fruitful: the fact that fullerenes behave chemically as electron deficient super-alkenes [3] is essentially a graph-theoretically determined consequence of the fact that the typical adjacency spectrum has more positive than negative eigenvalues. In spite of previous work, explicit mathematical characterisation of important electronic substructures and properties (open and closed-shells, distortive electronic configurations, conditions for the existence of non-bonding orbitals (zero eigenvalues), fully distributed spin populations (nut graphs), eigenvalues of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), ...) is still an open question for many chemically important classes of graph.

Single-molecule Conduction: An entirely new arena for application of chemical graph theory has opened up in the past few years, in the shape of the tight-binding theory of ballistic conduction in molecular electronic devices. The physics of conduction of an electron through a

molecule attached with atomic resolution to wires can be modelled by adjacency-matrix theory with open-system boundary conditions. The basic equation for the transmission of such systems as a function of the energy of the incoming electron has been derived and cast in terms of characteristic polynomials of the molecular graph and vertex-deleted sub-graphs [4]. Theorems from graph theory then allow prediction of transmission for composite devices [5], which should be generalisable to the large and eventually infinite graphs that describe conducting polymers.

1.2 Methodologies

This will involve modelling stability, dynamics and properties using tools established by us and others for fullerenes, but will critically depend on the expertise of the other PIs. A programme of classification of types of universal conduction classes of graphs will also be established.

2 Information on funding

2007-2010 University of Sheffield, Two Phd studentships, one working on molecular conduction, one on ring currents in aromatic molecules. Nominal value 80,000 GBP

References

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