Theoreticians finally prove that 'curly arrows' tell the truth about chemical reactions

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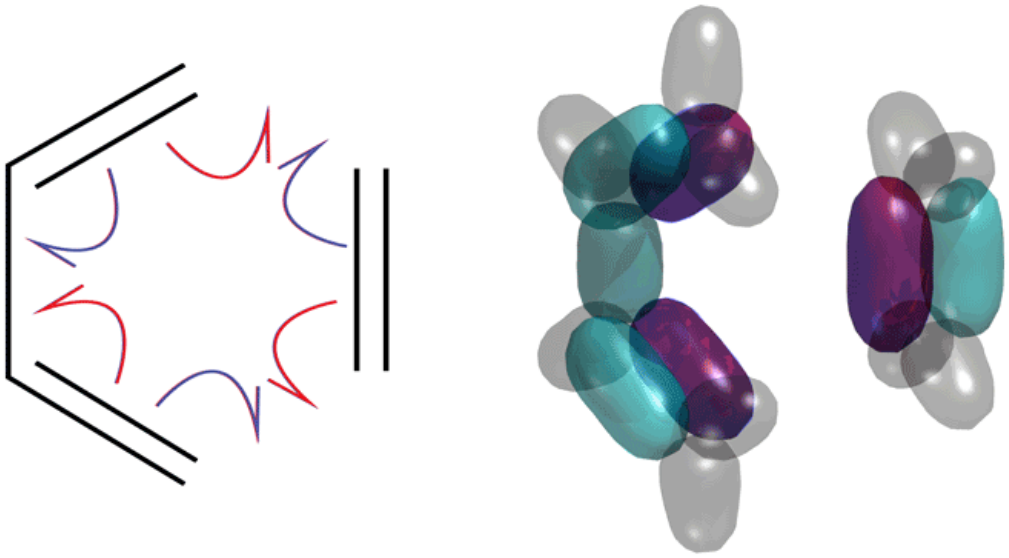


The Diels-Alder reaction is important in the synthesis of all sorts of pharmaceuticals, including vitamin D. But how does it work? UNSW researchers show that it involves the splitting of electron pairs. Credit: T. Schmidt

Recent work from the ARC Centre of Excellence in Exciton Science, published in *Nature Communications* today, bridges the cultural gap between organic chemists and theoreticians that is embodied in the "curly arrow."

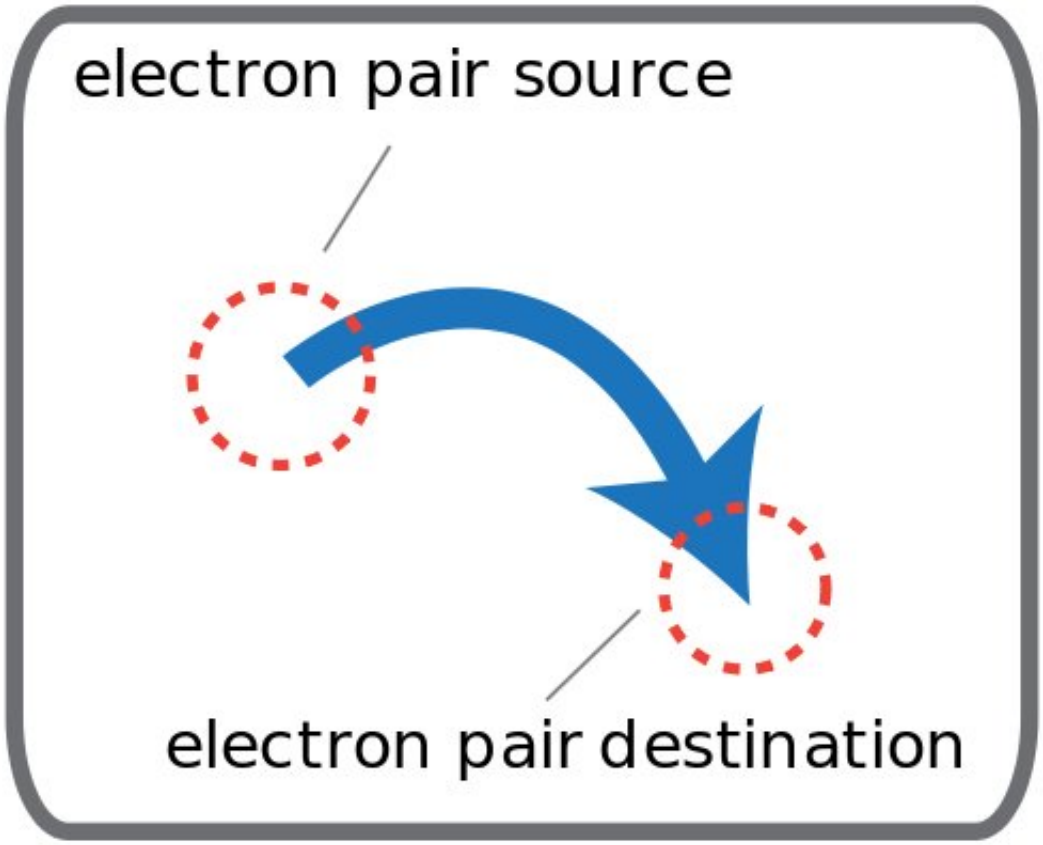
The research team is led by UNSW Sydney Professor Timothy Schmidt and includes UNSW Canberra's Dr Terry Frankcombe and Dr Philip Kilby from CSIRO's Data61.

Organic chemists use curly arrows to depict the way chemical reactions occur and the resulting molecular structures. Theoreticians tend to talk about structure of molecules in terms of molecular orbital theory (wave theory) and say that curly arrows are a fiction. The paper unites disparate views of electronic structure for the first time, helping to connect theory with organic chemistry notation.

The team used theoretical modelling, looking at the wave functions in new ways to show why curly arrows work.

"Previously, we knew that curly arrows work but we didn't know why," Professor Schmidt says.

Leader of Data61's Optimisation research group Dr Kilby, who used an optimisation procedure to reduce calculation time by two orders of magnitude, says "the UNSW researchers were able to devise a method that can estimate the probabilistic location of electrons as a chemical reaction actually takes place".



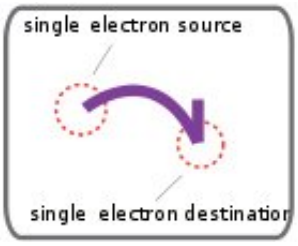
Arrow representing electron pair movement. Credit: creative commons

"This allows us to model chemical reactions in a more detailed way than has ever been possible before."

This unprecedented method of extracting the movements of electrons during a chemical reaction is a breakthrough in connecting traditional depictions of chemical mechanism with state-of-the-art quantum chemical calculations.

"We have shown how to relate rigorous calculations to the qualitative diagrams of organic chemists, in essence showing why they work," Schmidt explains.

According to Dr Frankcombe, "this work demonstrates that these classical, intuitive ideas of individual electron movements have been the right way to look at chemical reactivity all along, even though they previously had little support from quantum mechanics".



Fish hook arrow representing single electron movement. Credit: creative commons

More information: Yu Liu et al, Calculating curly arrows from ab initio wavefunctions, *Nature Communications* (2018). DOI: 10.1038/s41467-018-03860-2

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