Chemist tames longstanding electron computation problem

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(PhysOrg.com) -- When the University of Chicago's David Mazziotti talks about chemistry, perhaps he is thinking about how the behavior of all of the electrons in a molecule can be anticipated from the behavior of just two of its electrons.

For 50 years theoretical chemists have puzzled over the problem of predicting many-electron chemistry with only two electrons, which many thought intractable and perhaps impossible to solve. Mazziotti, an associate professor in chemistry, will present a new approach to tuning his solution to the problem for exceptional computational accuracy and efficiency in the Dec. 12 issue of *Physical Review Letters*.

"We can do all these calculations using a desktop computer," Mazziotti said. "We're getting accuracy and efficiency that supercedes some of the traditional techniques, so it really opens up a whole new ballgame."

Scientists have grappled with the problem for decades because a detailed statistical description of electrons' positions in a molecule can reveal whether a particular chemical reaction will occur. But the number of electrons in an atom or molecule can range from 10 to hundreds or thousands.

Even the most powerful computers lack the power to perform these calculations, which become increasingly expensive as more electrons are added to the mix. The computational cost stems from the laws of quantum mechanics, the branch of physics that governs the behavior of

atoms and molecules. Mazziotti's advance means that chemists will be able to compute the electronic properties of a given molecule with greater accuracy at a lower cost.

Mazziotti anticipates that his research tool will enable scientists to more rapidly solve a wide range of problems in chemistry, including the chemistry of free radicals. Free radicals are molecules with unpaired electrons that play a key role in reactions that deplete atmospheric ozone and create greenhouse gases. Radical-type reactions are also important in the design of new drugs and more efficient combustion engines.

Mazziotti began working on the problem of using two electrons to represent many electrons in the mid-1990s as a graduate student at Harvard University. His graduate school mentor, Nobel laureate Dudley Herschbach, has called the quest "a 'holy grail' of theoretical chemistry."

Speaking of Mazziotti's progress in 2006, Herschbach said that "David Mazziotti has made a major advance in fundamental theory."

Herschbach employed a football analogy to illustrate Mazziotti's method, known to theoretical chemists as the 2-electron Reduced Density Matrix (2-RDM) method.
In this analogy, a coach could automatically determine the actions of an entire team by simply plotting the motion of just two to three players: the quarterback and one running back/receiver, with auxiliary help from one lineman.

"His method requires dealing with just pairs and trios of electrons," Herschbach said.

The late Joseph Mayer, a professor in chemistry at the University of Chicago from 1946 until 1960, was one of the first scientists to propose doing electronic structure calculations for many-electron atoms and

molecules by using just two electrons.

In the 2-RDM approach, one determines the probabilities for finding a pair of electrons at different locations in an atom or molecule. But a problem arises, Mazziotti said. "If one wants to work with these two-electron distributions, one has to make sure that they actually represent the many-electron system adequately."

Mazziotti has in fact developed several two-electron approaches that target different levels of accuracy and efficiency. The previous approaches tuned for maximum accuracy have applications to highly challenging problems like bi-radicals (molecules with two unpaired electrons), electron-rich materials, and molecular conductivity.

The latest tool extends independent work by Christian Kollmar at the Zernike Institute for Advanced Materials in the Netherlands as well as work with University of Chicago graduate student Eugene DePrince. It is tuned for high efficiency and impressive accuracy for applicability to a very wide range of chemical problems.
"We view 2-RDM theory as a platform that we can now tune, essentially, to get high accuracy or high efficiency or some combination of both of those for different molecular systems," Mazziotti said.

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