New method edges closer to holy grail of modern chemistry

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University of Chicago chemist David Mazziotti has developed a new method for determining the behavior of electrons in atoms and molecules, a key ingredient in predicting chemical properties and reactions. He presented the details of his method in the Oct. 6 issue of the journal *Physical Review Letters*.

"In his new paper, David Mazziotti has made a major advance in fundamental theory," said Nobel laureate Dudley Herschbach, the Frank Baird Jr. Professor of Science at Harvard University. "It will surely find wide application."

The behavior of electrons in atoms and molecules affects many significant chemical reactions that govern everyday phenomena, including the fuel efficiency of combustion engines, the depletion of ozone in the atmosphere, and the design of new medicines. The importance of electrons in these and countless other chemical phenomena have led scientists since the 1950s to seek an efficient way to determine the distribution of electrons in atoms and molecules.

There can be hundreds or even thousands of electrons moving around the nuclei of a molecule--far too many for their distribution in the molecule to be determined exactly even with modern supercomputers. But during the 1950s, scientists realized that they could, in principle, use only a pair of electrons to represent any number of electrons accurately.

"That quest has been a 'holy grail' of theoretical chemistry for more than

50 years," Herschbach said. It's a problem that Mazziotti first tackled as a Ph.D. student working with the encouragement of Herschbach at Harvard in the late 1990s. And now, "he has developed and demonstrated the accuracy of an innovative approach that brings him much closer to the holy grail than anyone has managed to get before," Herschbach said.

If applied to football, Herschbach explained, Mazziotti's highly complex work would mean that the Chicago Bears offense could operate with just one quarterback and one running back/pass receiver, with auxiliary help from just one lineman. Plotting the roles of just three players would automatically determine the actions of the entire team. "His method requires dealing with just pairs and trios of electrons," Herschbach said.

Mazziotti's work has its roots in the Schrödinger equation. Formulated in 1925 by Erwin Schrödinger, the equation is the primary equation of quantum mechanics. "While the equation determines the behavior of all the electrons in an atom or molecule, the computational cost of its solution increases exponentially with the number of electrons," Mazziotti explained.

In 1976, scientists produced a contracted Schrödinger equation that depends upon only four of a molecule's electrons. Solution of the contracted Schrödinger equation remained elusive until Carmela Valdemoro at the Consejo Superior de Investigaciones Cientificas in Spain recognized in 1993 that the behavior of the remaining four electrons could be expressed in terms of just two electrons. "The first successful calculations were her calculations," Mazziotti said.

As a graduate student in the late 1990s, Mazziotti verified and extended Valdemoro's work, as did Kyoto University's Hiroshi Nakatsuji. Accuracy, however, remained an issue until Mazziotti's current advance. Results that formerly ranged from 71 to 96 percent accuracy have

jumped to 95 to 100 percent. The contracted Schrödinger equation may soon become solvable with a package of computer software, according to Mazziotti.

But first will come a book edited by Mazziotti that will provide other scientists a roadmap for his field of study. Mazziotti solicited articles from an international group of scientists. His book, Two-Electron Density Matrix Mechanics for Many-Electron Atoms and Molecules, will be published by John Wiley and Sons in the Advances in Chemical Physics series in early 2007.

The work is complicated, as the title suggests. "But it's fun and we're getting much better at doing it," Mazziotti said.

Source: University of Chicago