

Quantum Theory Project Löwdin Lecture
Wednesday, January 21, 2009 from 3:30 to 4:30 PM
2205 New Physics Building

TRACTABLE VALENCE SPACE METHODS
FOR STRONG ELECTRON CORRELATIONS

2009 Löwdin Lecture

Martin Head-Gordon
University of California, Berkeley

QTP Seminar

3:30 - 4:30 PM, Wednesday, January 21, 2009
2250 New Physics Building

Chemistry Departmental Colloquium

4:00 - 5:00 PM, Friday, January 23, 2009
CLB C130

Reception immediately following the colloquium

5:00 - 6:00 PM

Wave function-based quantum chemistry has two traditional lines of development – one based on molecular orbitals (MO's), and the other on valence bond (VB) theory. Both offer advantages and disadvantages for the challenging problem of describing strong correlations, such as the breaking of chemical bonds, or the low-spin (antiferromagnetic) coupling of electrons on different centers.

Within MO methods, strong correlations can be viewed as those arising within a valence orbital active space. One reasonable definition of such a space is to supply one correlating orbital for each valence occupied orbital. Exact solution of the Schrödinger equation in this space is exponentially difficult with its size, and therefore approximations are imperative. The most common workaround is to truncate the number of orbitals defining the active space, and then solve the truncated problem, as is done in CASSCF. An important alternative is to systematically approximate the Schrödinger equation in the full valence space, for example by using coupled cluster theory ideas. I shall discuss progress in this direction.

Within spin-coupled VB theory, the target wave function consists of a set of non-orthogonal orbitals, one for each valence electron, that are spin-coupled together into a state of the desired overall spin-multiplicity. The number of active orbitals is identical with the valence space MO problem discussed above, though the problem is not identical. Exact solution of the VB problem is exponentially difficult with molecular size, and therefore approximations are imperative. Again, the most common approach is to seek the exact solution in a truncated valence orbital space, where other orbitals are simply treated in mean-field. It is possible, however, to also consider approximations that do not truncate the space, but rather reduce the complexity. A new way of doing this will be introduced and contrasted with the MO-based approaches.

Chemistry Colloquium
Friday, January 23, 2009 from 4:00 to 5:00 PM
130 Chemistry Lab Building

INTRA AND INTERMOLECULAR INTERACTIONS PROBED
BY ELECTRONIC STRUCTURE THEORY CALCULATIONS

This talk will cover some recent developments in practical density functional theory (DFT) calculations and how to analyze such calculations. With respect to DFT calculations, the latest developments in density functionals will be discussed. The chemical bonding and redox properties of some remarkable dicopper diphosphorus diamondoids will be discussed as a case study of intramolecular interactions. With respect to analyzing intermolecular interactions, a useful decomposition scheme is introduced which gives particular insight into the nature of dative interactions. We discuss a variety of examples ranging from hydrogen bonding to ligand-metal interactions, where our methods sometimes confirm conventional wisdom and sometimes strongly contradict previous interpretations.

Reception immediately following Colloquium
from 5:00 to 6:00 PM

A Brief Biography

Martin Head-Gordon is a professor of chemistry at the University of California, Berkeley and a faculty chemist at the Lawrence Berkeley National Laboratory. He received his B.Sc. (1983) and M.Sc. (1985) from Monash University and Ph.D. from Carnegie Mellon University in 1989 under the supervision of Sir John A. Pople (Nobel Laureate, 1998). Martin spent subsequent 3 years as a postdoctoral fellow at Bell Laboratories, working with John Tully, until he was appointed as an assistant professor at Berkeley in 1992, where he quickly rose to the ranks of associate (1997) and full professor (2000).

Martin is universally regarded as the leader in the field of electronic structure theories, especially the development and applications of novel mathematical methods that permit the treatment of problems that are beyond the reach of standard methods. Martin made many breakthrough contributions to various aspects of electronic structures, ranging from molecular integral evaluation, linear-scaling methods, perturbation and coupled-

cluster theory, density-functional theory to computational applications in interstellar and biochemistry.

Martin has over 300 publications of which at least 30 are cited by 100 other publications and 4 are cited by over 1,000 publications. Martin was instrumental in the development of the CCSD(T) (coupled-cluster singles and doubles with a non-iterative triples) theory, considered the gold standard of electron correlation theory, modern CIS (configuration-interaction singles) theory, the Gaussian-1 composite method, the algorithms of MP2 (second-order Moeller-Plesset perturbation) theory, continuous fast multipole method for linear scaling density functional theory, etc., thus garnering his "highly cited" status of the ISI Web of Knowledge citation database.

Martin received National Science Foundation Young Investigator Award (1993-98) and Annual Medal of the International Academy of Quantum Molecular Science (1998). He was also an Alfred P. Sloan Research Fellow (1995-97), Joel H. Hildebrand Chair in Chemistry (1994-96), David and Lucille Packard Fellow (1995-2000), and Miller Research Professor (2001-02). Martin is known for his excellence in teaching and mentoring, serving as Vice-Chair of Teaching in the Department of Chemistry and also winning the Departmental Teaching Award (2001) and many of his group members went on to become faculty members of universities including University of Southern California, Georgia Tech, Rutgers, Cornell, Mississippi State University, University of Florida, MIT, University of Michigan, Harvard, University of Mississippi, etc.

He is a member of editorial advisory boards of International Journal of Quantum Chemistry, Journal of Theoretical and Computational Chemistry, Journal of Physical Chemistry, and Physical Chemistry Chemical Physics and also serves as the Chair of Theoretical Chemistry Subdivision of American Chemical Society, organizing many of the National ACS Meetings. Martin is also a co-founder of Q-Chem, Inc. and one of the main architects of the computational chemistry software Q-Chem, which is widely used in academia and industry.

