

James F. Harrison

## Quantum Chemistry

### PROFESSOR

(b. 1940)  
 B.S., 1962,  
 Drexel Institute of Technology;  
 M.A., 1964,  
 Princeton Univ.;  
 Ph.D., 1966,  
 Princeton Univ.;  
 NSF Postdoctoral Fellow, 1966-67,  
 Research Associate, 1967-68,  
 Indiana Univ.;  
 Scientist in Residence, 1980-81  
 Argonne National Laboratory.

517-355-9715,  
 Ext. 295

### SELECTED PUBLICATIONS

*Electronic Structure of Diatomic Molecules Composed of a First-Row Transition Metal and Main-Group Element (H-F)*, J. F. Harrison, *Chem. Rev.* **2000**, *100*, 679-716.

*Dipole and quadrupole moment functions of the hydrogen halides, HF, HCl, HBr, and HI: A Hirshfeld interpretation*, J. F. Harrison, *Journal of Chemical Physics* **2008**, *128*, 114320.

*Collision-Induced dipoles and Polarizabilities of Pairs of Hydrogen Molecules: Ab Initio Calculations and Results from Spherical Tensor Analysis*, X. Li, J. F. Harrison, M. Gustafsson, F. Wang, M. Abel, L. Frommhold, and K. L. C. Hunt, *Proceedings of the ICCMSE* **2009**.

*A Hirshfeld interpretation of the charge, spin distribution, and polarity of the dipole moment of the open shell  ${}^3\Sigma^-$  nitrogen halides: NF, NCl, and NBr*, J. F. Harrison, *Journal of Chemical Physics* **2009**, *131*, 044117.

"Methylene: A Personal Perspective", James F. Harrison, pages 33-43, "Advances in the Theory of Atomic and Molecular Systems: Conceptual and Computational Advances in Quantum Chemistry" Edited by P. Piecuch, J. Maruani, G. Delgado-Barrio, and S. Wilson, Springer 2009

*Ab Initio Investigation of Titanium Hydroxide Isomers and their Cations, (H-Ti-O) $^0$  and (Ti-O-H) $^0$* , Milordos E, Harrison J. F. and Hunt K. L. C., *J. Chem. Phys.* **2011**, *135*, 144111.

*A Hirshfeld interpretation of the local moment composition of the quadrupole moments of the halogenated acetylenes FCCF, ClCCCl, BrCCBr, and ICCL*, J. F. Harrison, *Computational and Theoretical Chemistry* **2012**, *999*, 83-88.

*The ground and excited states of vanadium hydroxide isomers and their anions and cations, (V-OH) $^{0-}$  and (H-V-O) $^{0-}$* , Milordos E, Harrison J. F. and Hunt K. L. C., *J. Chem. Phys.* **2013**, *138*, 114305.

*Hirshfeld density partitioning technique: A first application to the transition metal compounds, HScO, TiO and VO*, Milordos E and Harrison J. F., *J. Chem. Phys.* **2013**, *138*, 184305-7.

# ADVANCES IN FUNDAMENTAL THEORY

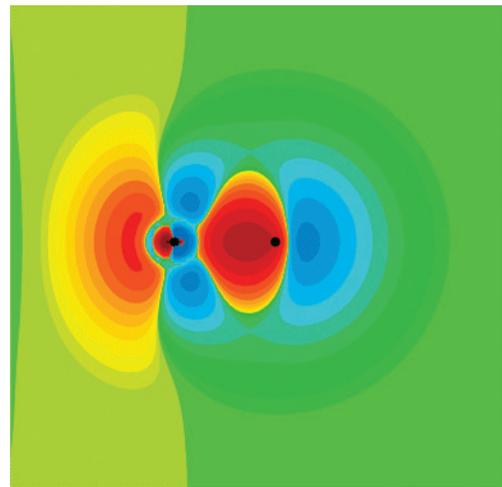
and computer technology enable us to construct wavefunctions for atoms and molecules which are of unprecedented accuracy. We use these functions to assist in the interpretation of spectroscopic experiments and to develop and refine the qualitative notions of chemical bonding. Our current focus is to understand:

### **The electronic structure of the ground and low-lying states of small molecules containing a transition metal atom.**

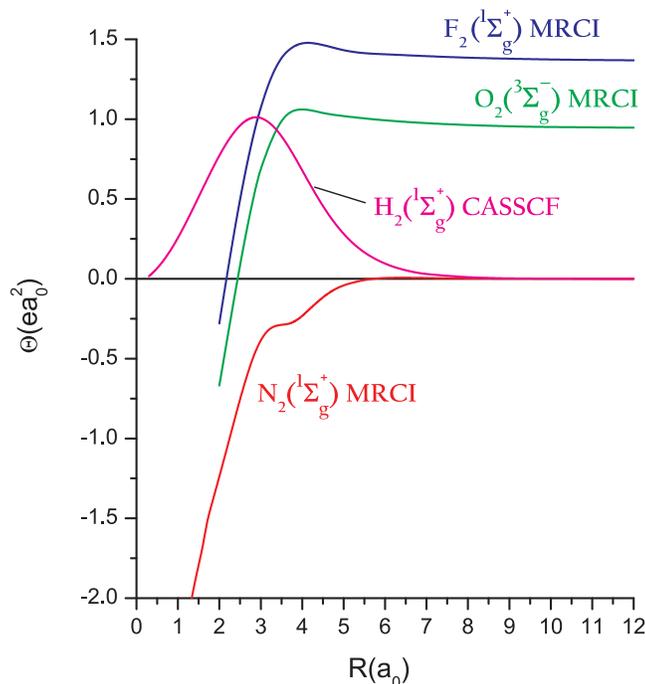
Diatomics of interest include MX where M is a transition metal (Sc to Zn) and X is a main group element (H to Cl). These molecules are of great interest as models for the nature of the transition meta-main group element chemical bond. Triatomics include the metal hydroxides MOH & HMO and the carbynes MCH, the understanding of which is fundamental to the reactions of transition metals with hydrocarbons. We are also interested in the structure of the mono- and dipositive ions of these systems.

### **The nature of molecular multipole moments and the information contained in these moments about the chemical bond.**

While we all have an instinctive feeling about the meaning of a molecular dipole moment and how it reflects the charge distribution in a molecule the same instincts often fail when considering for example, the quadrupole moment. Some of this problem is that the quadrupole moment is a second rank tensor while the dipole moment is a tensor of the first rank. However even for homonuclear diatomics



Electron density map of the  ${}^1\Sigma^+$  state of HCl calculated using a CASSCF wavefunction and the  $qvz$  basis set.



Molecular quadrupole moments as a function of bond length.

**The spatial distribution of electron spin in open shell molecules.** We have recently shown in the open shell nitrogen halides, NF, NCl and NBr that  $\alpha$  and  $\beta$  spins flow in opposite directions as the chemical bond forms. We are exploring this observation and the role that electronegativity (chemical potential) plays.  $\blacklozenge$

where the quadrupole tensor has only one unique component the relationship between this component and the molecular charge density is not well understood. We have recently shown that the molecular quadrupole moment can be written as the sum of the quadrupole moments of the constituent atoms plus a term that depends on the shift in the electron density upon bond formation. In the course of this work we have defined the quadrupole moment density that shows where in the molecule the molecular contribution to the quadrupole moment comes from. We are extending these ideas to other one electron properties like the electric field gradient at a particular nucleus and the dipole moment (still more to learn!).