# Selective research survey of Klaus Ruedenberg

## *I. Innovations in ab-initio methodologies*

● The breakthrough in the evaluation of previously held prohibitive electronic repulsion energies, created the unique capability required for Mulliken's group to be successful in their seminal pioneering of ab initio quantum chemistry in the 1950's.

- *A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. II. The Two-Center Exchange Integrals.* K. R., J. Chem. Phys. *19*, 1459-1477 (1951*)*,
- *Progress Report on the Investigation of Integrals between Slater Atomic Orbitals and their Application in Molecular Calculations,* K.R. in Technical Report 1952-1953, II. (Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, 1953). pp 14-21
- *Two-Center Electron Interaction Energies*, K.R. in "Molecular Orbitals in Chemistry, Physics and Biology, (PO. Löwdin and B. Pullman, Edtrs, Academic Press, 1964) pp. 215-225.

● Conception of the full molecular reaction space wave functions and demonstration of their usefulness for the prediction of bonding energies.

- *MCSCF Studies of Chemical Reactions I. Natural Reaction Orbitals and Localized Reaction Orbitals*, KR & K. Sundberg on pp. 505-515 of "Quantum Science" (J.L. Calais, O. Goscinski, J. Linderberg, Y. Öhrn, Edtrs, Plenum Publ. N.Y. 1976).
- *Dimerization of Carbene to Ethylene*, L.M. Cheung, K.R. Sundberg & KR, J. Am. Chem. Soc. *100*, 8024 (1978)
- *Electronic Rearrangements During Chemical Reactions II. Planar Dissociation of Ethylene,* L.M. Cheung, K.R. Sundberg & KR, Int. J. Quant. Chem. *16*, 1103-1137 (1979).
- KR, *Determination of Orbitals and Selection of Configurations Through the Method of the Full Optimized Reaction Space*, KR on pp 46-64 of "Report on the NRCC 1978 Workshop on Post-Hartree-Fock Quantum Chemistry", (Lawrence Berkeley Laboratory, Univ. of California, Report LBL 8233, UC4, CONF 780883)

Professor B. Roos of Lund University, Sweden, a participant in this workshop, has stated that KR's presentation influenced him to implement full reactions space wave functions using the "direct CI", then being developed in Sweden, for the configuration interaction part. This combination yielded the CASSCF method of 1980, which enabled applications beyond small molecules.

● Development of effective multi-configuration self-consistent-field (MCSCF) methods.

- *MCSCF Optimization Through Combined Use of Natural Orbitals and the Brillouin-Levy-Berthier Theorem,* KR, L.M. Cheung & S.T. Elbert, Int. J. Quant. Chem. *16*, 1069 (1979)
- *An MCSCF Method for Ground and Excited States Based on Full Optimizations of Successive Jacobi Rotations,* J.Ivanic and KR, J. Computational Chemistry 24, 1250-1262 (2003)

● Discovery of the Correlation Energy Extrapolation through Intrinsic Scaling (CEEIS), the only existing procedure for recovering full configuration interaction energies. Notably, it is also valid for multi-configurational reference functions and has yielded potential energy curves of spectroscopic accuracy, as cited below under III.

- *Correlation Energy Extrapolation through Intrinsic Scaling. IV. Accurate Binding Energies of the Homonuclear Diatomic Molecules Carbon, Nitrogen, Oxygen and Fluorine.* L. Bytautas & KR,. J. Chem. Phys., *122*, 154110 (2005*)*

● Development of the even-tempered optimization of primitive atomic orbital sets. The effectiveness of this orbital exponent organization has proven to be invaluable for the construction of atomic orbital bases, the crucial back bone of molecular ab initio calculations.

- *Systematic Approach to Extended Even-tempered Orbital Bases for Atomic and Molecular Calculations*, D.F. Feller & KR, Theor. Chim. Acta, *52*, 231-251 (1979)
- *Effective Convergence to Complete Orbital Bases and to the Atomic Hartree-Fock Limit through Systematic Sequences of Gaussian Primitives.* M.W. Schmidt & KR, J. Chem. Phys., *71*, 3951-3962 (1979)

● A viable algorithm was devised for generating the configurational transformation that is induced by an orthogonal orbital transformation in a configuration interaction expansion.

- *Orbital Transformations and Configurational Transformations of Electronic Wave Functions*, G.J. Atchity and KR, J. Chem. Phys. *111*, 2910-2920 (1999)

● Development of the effective parametrization of a general orthonormal transformation in terms of independent variables.

- *Generalization of Euler Angles to N-Dimensional Orthogonal Matrices*, D.K. Hoffman, R.C. Raffenetti and KR, J. Mathem. Phys., *13*, 528-532 (1972).

● The only viable way for the efficient evaluation of the rotation matrices of spherical harmonics, which are needed for atomic orbital rotations, was devised (Wigner's classical formulas being impractical). This algorithm has become essential for all 3D-type video animations, where it has been universally incorporated in the codes that create the required differentiating shadows from an assumed light source.

- *Rotation Matrices for Real Spherical Harmonics. Direct Determination by Recursion*, J. Ivanic & KR, J. Phys. Chem. *100*, 6342-6347 (1996)
- *Rapid and Stable Determination of Rotation Matrices between Spherical Harmonics by Direct Recursion*, Cheol Ho Choi, J. Ivanic, M.S. Gordon & KR, J. Chem. Phys, *111*, 8825-8831 (1999)

## II. Identification and quantification of atoms and bonding synergism inherent in accurate molecular ab-initio wave functions

The aim of this work is the recovery of the chemical model of atoms and bonds in molecules from the actual molecular ab initio electronic wave functions without positing additional model wave functions.

● The first rigorous resolution of the full molecular electronic ab initio energy as a sum of intra-atomic energy increases, coulombic interactions and bonding interferences. Identification of the kinetic energy lowering by delocalization as the cause of binding in $H_2$.

- *The Physical Nature of the Chemical Bond.* KR, Rev Mod Phys. *34*, 326-376 (**1962**). (Among the 100 most quoted papers in Rev Mod Phys. 1955-88)

● The first viable method for quantitatively recovering localized orbitals intrinsic to ab-initio wave functions. It stimulated a large literature on further theory and on applications to gain manifold chemical insights.

- *Localized Atomic and Molecular Orbitals.* C. Edmiston & KR, Revs. Modern Phys. *35,* 457-465 (**1963**) (Among the 100 most quoted papers in Rev. Mod. Phys. 1955-1988).
- *Localized Molecular Orbitals: A Bridge between Chemical Intuition and Molecular Quantum Mechanics,* W. England, L. S. Salmon & KR, Topics in Current Chemistry *23,* 31-123 (1971)

**-** and many other publications

• Calculations using new localized orbitals invalidate the dogma, which was commonly assumed for half a century, that natural orbitals generate the most rapid configuration interaction convergence.
> **-** *Split-Localized Orbitals Can Yield Stronger Configuration Interaction Convergence than Natural Orbitals*, L. Bytautas, J. Ivanic and KR J. Chem. Phys. 119, 8217 (2003)

• Recognition and documentation that the optimized full molecular valence space is dominant for the essential interactions that contribute to the bonding synergism.
> **-** *Are Atoms Intrinsic to Molecular Wave Functions? I. The FORS Model.* KR, M.W. Schmidt, M.M. Gilbert, S.T. Elbert*, Chemical Physics 71,* 41-49 (1982).
> **-** *Are Atoms Intrinsic to Molecular Electronic Wave Functions? II. Analysis of FORS Orbitals,* KR, M.W. Schmidt, M.M. Gilbert*, Chemical Physics 71, 51-*64 (1982).
> **-** *Are Atoms Intrinsic to Molecular Electronic Wave Functions? III. Analysis of FORS Configurations,* KR, M.W. Schmidt, M.M. Gilbert, S.T. Elbert*, Chemical Physics 71,* 65-78 (1982).
> **-** *Intra-Atomic Correlation Correction in the FORS Model,* M. T. B. Lam, M. W. Schmidt & KR, J. Phys. Chem. *89,* 2221-2235 (1985).
> **-** *Chemical Binding and Electron Correlation in Diatomic Molecules as Described by the FORS Model and the FORS-IACC Mode*l, M.W. Schmidt, M.T.B. Lam, S.T. Elbert & KR Theor. Chim. Acta, 68, 69-86 (1985)

• Demonstration that the ab-initio-optimized full *molecular* valence space can be spanned by molecular orbitals that are extremely close to optimized minimal-basis orbitals of the constituent *free* atoms, the "quasi-atomic" orbital (QUAO) basis for the molecule.
> **-** *Molecule Intrinsic Minimal Basis Sets. I. Exact Resolution of Ab-Initio Optimized Molecular Orbitals in terms of Deformed Atomic Minimal-Basis Orbitals,* W.C. Lu, C.Z. Wang, M.W. Schmidt, L. Bytautas, K.M. Ho & KR*, J. Chem. Phys.120,* 2629-2636 (2004*)*
> **-** *Molecule Intrinsic Minimal Basis Sets. II. Bonding Analyses for $Si_4H_6$ and $Si_2$ to $Si_{10}$,* W.C. Lu, C.Z. Wang, M.W. Schmidt, L. Bytautas, K.M. Ho & KR*, J. Chem. Phys. 120,* 2638-2651 (2004)
> **-** *Exact Representation of Electronic Structures in Crystals in Terms of Highly Localized Quasiatomic Minimal Basis Orbitals*, W.C. Lu, C.Z. Wang, T.L. Chan, KR & K.M. Ho, Phys. Rev. B, *70,* 04110(R) (2004)
> **-** *Intrinsic Local Constituents of Molecular Electronic Wave Functions. Exact Representation of the Density Matrix in terms of Chemically Deformed and Oriented Atomic Minimal Basis Set Orbitals. I* J. Ivanic, G.J. Atchity & KR, Theor. Chem. Acc. *120,* 281 & 295 (2008)
> **-** *Intrinsic Local Constituents of Molecular Electronic Wave Functions. II. Electronic Structure Analyses in terms of Intrinsic Oriented Quasi-Atomic Molecular Orbitals for the Molecules FOOH, $H_2BH_2BH_2$, $H_2CO$ and the Isomerization HNO$\rightarrow$NOH.* J. Ivanic and KR, Theor. Chem. Acc.*, 120,* 295-305 (2008)

• The expansion of the molecular ab initio density matrices in terms of quasi-atomic orbitals yields a resolution of the interatomic interference energies, which have been shown to reveal the bonding patterns in molecules and along reaction paths. A novel measure of the bonding drive, the *kinetic bond order*, was formulated and has proven effective in identifying bonding motifs, notably elucidating uncommon motifs that present challenges to conventional intuition.
> **-** *A comprehensive analysis of molecule-intrinsic quasi-atomic, bonding and correlating orbitals. I. Hartree-Fock wave functions,* A.C.West, M.W.Schmidt, M.S.Gordon & KR*, J. Chem. Phys 139,* 234107 (2013*)*

- *A comprehensive analysis in terms of molecule-intrinsic, quasi-atomic orbitals. II. Strongly correlated wave functions,* A.C. West, M.W. Schmidt, M.S. Gordon & KR*, J. Phys. Chem. A 119,* 10360 (2015)
- *A comprehensive analysis in terms of molecule-intrinsic, quasi-atomic orbitals. III. The covalent bonding structure of urea.* A.C. West, M.W. Schmidt, M.S. Gordon & KR*, J. Phys. Chem. A 119,* 10368 (2015)
- *A comprehensive analysis in terms of molecule-intrinsic quasi-atomic orbitals. IV. Bond breaking and bond forming along the dissociative reaction path of dioxetane.* A.C. West, M.W. Schmidt, M.S. Gordon & KR*, J. Phys. Chem. A 119,* 10376 (2015)
- *Identification and characterization of molecular bonding structures by ab initio quasi-atomic orbital analyses,* A.C. West, J.J. Duchimaza-Heredia, M.S. Gordon, & KR*, J. Phys. Chem. A, 121,* 8884 (2017)
- *Quasi-Atomic Bonding Analysis of Xe-Containing Compounds.* J.J. Duchimaza Heredia, KR & M.S. Gordon*, J. Phys. Chem. A, 122,* 3442 (2018)
- *Quasi-atomic bond analyses in the sixth period. II. Bond analyses of cerium oxides,* G.S. Schoendorff, M.W. Schmidt, KR & M.S. Gordon*, J. Phys. Chem. A, 123,* 5249 (2019*)*
- *Multiple bonding in rhodium monoboride. Quasi-atomic analyses of the ground and low-lying excited states,* G. Schoendorff, KR & M. S. Gordon*, J. Phys. Chem. A, 125,* 4836 (2021)

• Kinetic bond orders are effective in elucidating bond patterns because covalent bonding is driven by the kinetic interference energy lowering that results from interatomic electron sharing, a causality that has been analyzed in depth.

- *The Origin of Binding and Antibinding in the Hydrogen Molecule Ion,* M. J. Feinberg, KR & E. Mehler, on pp 27-98 of Advances in Quantum Chemistry Vol. 5, Editor, Academic Press, 1970)
- *Covalent bonds are created by the drive of electron waves to lower their kinetic energy through expansion.* M. W. Schmidt, J. Ivanic & KR, J. Chem. Phys. 140, 204104, (2014)
- *The physical origin of covalent binding,* M. W.Schmidt, J. Ivanic & KR, on pp 1−67 in *The chemical bond. Fundamental aspects of chemical bonding* (G. Frenking and S. Shaik Editors.; Wiley-VCH, Weinheim, Germany, 2014)

• By internal quasi-atomic transformations of the molecular wave function, the full ab initio valence space energy is reorganized so that the energy of formation of a molecule quantitatively becomes the result of a synergism between atomic promotions energies, quasi-classical Coulombic energies, non-classical Coulombic energies, Coulombic charge transfer energies, and electron sharing energies. In distinction from conventional approaches, no preconceived separate additional model wave functions are invoked.

- *Intrinsic resolution of molecular electronic wave functions and energies in terms of quasi-atoms and their interactions* A.C. West, M.S. Gordon & KR,, J. Phys. Chem, A, 121, 1086 (2017)
- *Why is $Si_2H_2$ not linear? An intrinsic quasi-atomic bonding analysis.* E. B. Guidez, M.S. Gordon & KR, J. Am. Chem. Soc., *142,* 13729 (2020)
- *Atoms and interatomic bonding synergism inherent in molecular electronic wave functions,* KR, J. Chem. Phys. Submitted

## III. Determination and analyses of potential energy surfaces

• The first exhaustive quantitative analysis of a global potential energy surface governing a polyatomic reaction mapped out in the entire 3-coordinate reaction space, embedded in 12 fully optimized spectator coordinates, settled basic questions regarding the carbene mechanism, notably the stereospecificity and the progress on the reaction path.

- *The Ring Opening of Cyclopropylidene to Allene. Global Features of the Reaction Surface,* P. Valtazanos, S.T. Elbert, S. Xantheas & KR*., Theor. Chim. Acta, 78*, 287-326 (**1991***),* and subsequent papers.*.*
- *The Ring Opening of Cyclopropylidene to Allene: Key Features of the Accurate Reaction Surface.* P. Valtazanos, S. Xantheas, S.T. Elbert & KR, Theor. Chim. Acta, *78*, 365-396 (1991).
- *The Ring Opening of Substituted Cyclopropylidene to Substituted Allene: The Effect of Steric and Long-Range Electrostatic Interactions*, P. Valtazanos and KR, Theor. Chim. Acta, *78*, 397-416 (1991).

• The conical intersection between two closed-shell states of like symmetry in ozone, one being the ground state was discovered and its existence incontrovertibly proved through the quantitative demonstration of the phase reversal, the first for a high-accuracy wave function. This discovery invalidated the widespread belief in the validity of the weak non-crossing rule. The global intersection seam was quantitatively identified and shown to form a multi-connected network containing intersections of intersection seam branches, the first such observation. These observations stimulated wider interest in and work on the importance of conical intersections.

- *Potential Energy Surfaces of Ozone. I.* S.S. Xantheas, G.J. Atchity, ST. Elbert & KR, J. Chem. Phys., *94*, 8054 (1991).
- *The Global Intersection Seam between the Lowest Two $^1A'$ States of Ozone*, G.J. Atchity, KR & A. Nanayakkara. Theor. Chem. Acc. *96*, 195-204 (1997)
- *Violation of the Weak Non-Crossing Rule between Totally Symmetric Closed Shell States in the Valence-Isoelectronic Series $O_3$, $S_3$, $SO_2$, $S_2O$.* G.J. Atchity, J. Ivanic, KR, J. Chem.Phys., *107*, 4307-4317 (1997).

• Using the CEEIS method (cited above under I) to obtain the full non-relativistic configuration interaction energy and adding the relativistic corrections, the only *global* theoretical potential energy curve of $F_2$ was obtained with an accuracy sufficient to calculate all 22 vibrational levels within less than 10 wave numbers from the experimental values. Subsequent investigations obtained analogous results for $O_2$, $C_2$ $B_2$ and complemented the experimentally incomplete spectra.

- *Accurate Ab Initio Potential Energy Curve of $F_2$. I. Non-Relativistic Full Valence CI Energies by the CEEIS Method.* L. Bytautas, T. Nagata, M. S. Gordon & KR, J. Chem. Phys. *127*, 164317, 1-18 (2007)
- *Accurate Ab Initio Potential Energy Curve of $F_2$. II. Core-Valence Correlations, Relativistic Contributions and Long-Range Interactions.* L. Bytautas, N. Matsunaga, T. Nagata, M. S. Gordon & KR, J. Chem. Phys. *127*, 204301, 1-12 (2007)
- *Accurate Ab Initio Potential Energy Curve of $F_2$. III. The Vibration Rotation Spectrum.* L. Bytautas, N. Matsunaga, T. Nagata, M. S. Gordon, K. Ruedenberg, J. Chem. Phys. *127*, 204313, 1-20 (2007).
- *Accurate ab initio potential energy curve of $O_2$. I. Non-relativistic full CI valence correlation by the CEEIS method,* L. Bytautas & KR, J. Chem. Phys. *132*, 074109, 1-10 (2010)
- *Accurate ab initio potential energy curve of $O_2$. II. Core-valence correlations, relativistic contributions and vibration-rotation spectrum*, L. Bytautas, N. Matsunaga & KR, J. Chem. Phys. *132*, 074307, 1-15 (2010)
- *Electronic structure analysis of the ground state potential energy curve of $Be_2$*, M.W. Schmidt, J. Ivanic & KR, J. Phys. Chem. A *114*, 8687-8696 (2010)
- *Accurate ab initio potential energy curves and spectroscopic properties of the four lowest singlet states of $C_2$,* J.S. Boschen, D. Theis, KR, & T.L. Windus, Theor Chem Acc *133*, 1425, 12 pages (2014)

• The first unified high-accuracy ab initio treatment covering the strong chemical short-range *as well as* the weak long-range interactions in a many-electron molecule was performed in $F_2$. It showed the first reported competition between a quadrupole-quadrupole ($r^{-5}$) repulsion and the dispersion ($r^{-6}$) attraction, resulting in a barrier of about 10 $cm^{-1}$ at about 3 time the equilibrium distance.

> - *Ab Initio Potential Energy curve of $F_2$. IV. Transition from the covalent to the van der Waals region. Competition between multipolar and correlation forces.* L. Bytautas & KR, J. Chem. Phys. *130*, 204101, 1-14 (2009)

• The determination and the quasi-atomic analysis of the linear, trans-bent and dibridged critical points on the potential energy surfaces of $C_2H_2$ and $Si_2H_2$ exhibited why, in $Si_2H_2$, the dibridged structure is more stable than the linear structure whereas, in $C_2H_2$, the opposite is the case. The reason is that, in $C_2H_2$, the lowest point on the PES is determined by the *interatomic* bonding interactions but, in $Si_2H_2$, it is determined by the *intra-atomic* promotion energy.

> - *Why is $Si_2H_2$ not linear? An intrinsic quasi-atomic bonding analysis.* E. B. Guidez, M.S. Gordon & KR, J. Am. Chem. Soc., *142,* 13729 (2020)

• Design of analyses and algorithms of basic potential energy surface features that are relevant for chemical reactions.

• *Quadratic* descent along a *gradient curve*

> - *Quadratic Steepest Descent on Potential Energy Surfaces. III. Minima Seeking along Steepest Descent Lines,* J. Q. Sun and KR, J. Chem. Phys. 99, 5276-5280 (1993), (Implemented in MOLPRO)

• Curves of gentlest ascent

> - *Gradient Extremals*, D. K. Hoffman, R. S. Nord, & KR, Theor. Chim. Acta, 69, 265-279 (1986)
> - *Gradient Extremals and Steepest Descent Lines on Potential Energy Surfaces,* J. Q. Sun & KR, J. Chem. Phys, 98, 9707-9714 (1993).

• Reaction path bifurcations are contingent on valley-ridge inflection points

> - *Bifurcations and Transition States,* P. Valtazanos & KR, Theor.Chimica Acta, *69*, 281-307 (1986)

• Exhaustive survey of possible gradient structures on potential energy surfaces near intersections

> - *Potential Energy Surfaces Near Intersections*, G.J. Atchity, S.S. Xantheas, & KR, J. Chem. Phys, *95*, 1862-1876 (1991)

• Demystification of the phase theorem by a local configurational analysis. Generalization of the phase theorem from isolated intersection seams to the case of intersecting intersection seam branches.

> - *A Local Understanding of the Quantum Chemical Geometric Phase Theorem for Potential Energy Surface Intersections*, G.J. Atchity & KR, J. Chem. Phys, *110*, 4208-4221(1999)

• The first method of forming diabatic states based on the continuity of their orbitals and their configurational expansions

> - *Determination of Diabatic States Through Enforcement of Configurational Uniformity*. KR & G. J. Atchity, Theor. Chem. Acc. *97*, 47-58 (1997)