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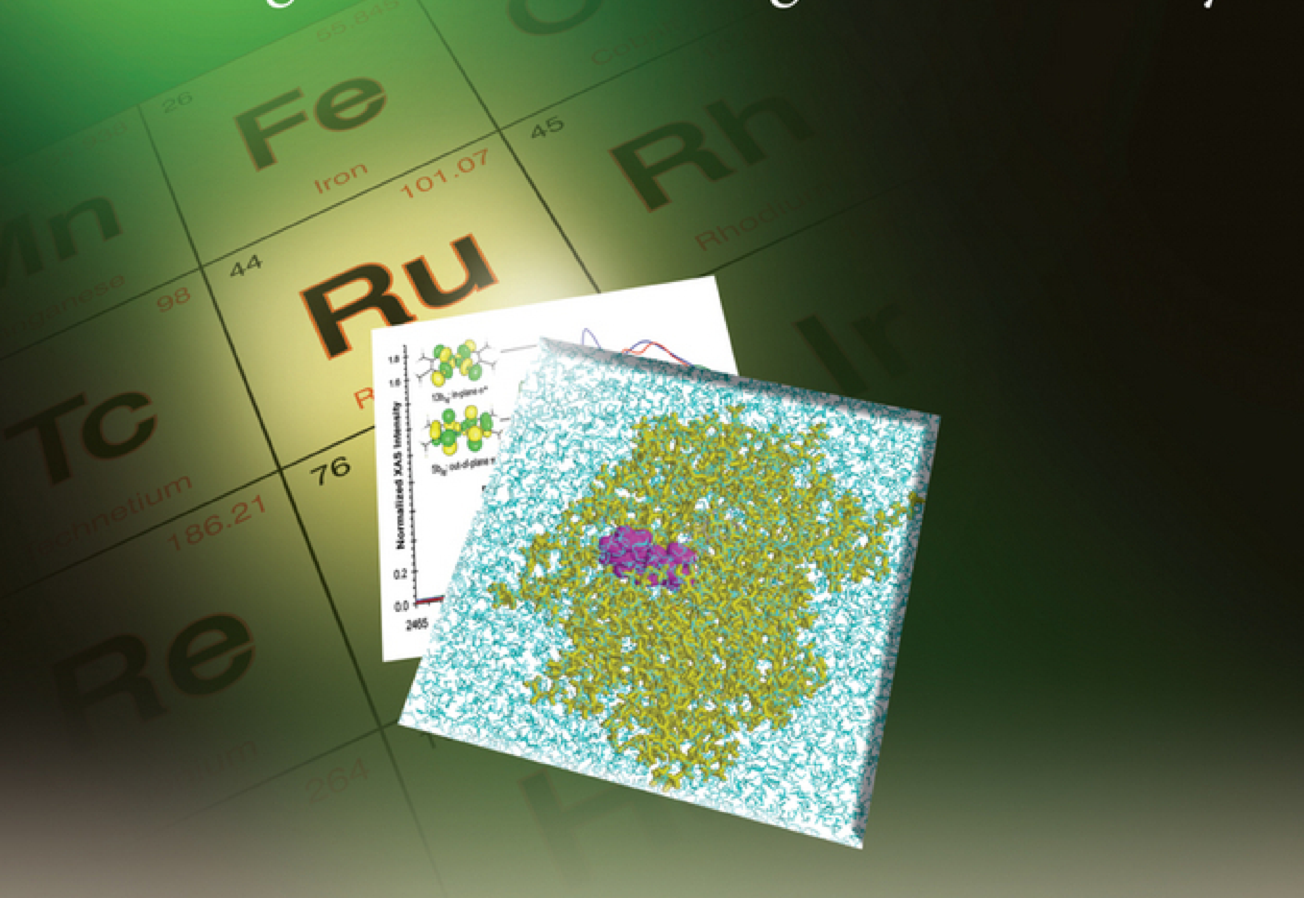
Edward I. Solomon • Robert A. Scott • R. Bruce King

Computational
Inorganic and Bioinorganic Chemistry



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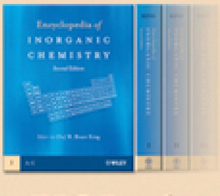

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Inorganic and Bioinorganic Chemistry

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Contents

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- Spectroscopic Properties Obtained from Time-Dependent Density Functional Theory (TD-DFT)

Mu-Hyun Baik
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- Computational Studies: Cisplatin

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- Hydrogenases: Theoretical Investigations Towards Bioinspired H_2 Production and Activation

Alexander I. Boldyrev
Utah State University, Logan, UT, USA
- Multiple Aromaticity, Multiple Antiaromaticity, and Conflicting Aromaticity in Inorganic Systems

Thomas C. Brunold
University of Wisconsin-Madison, Madison, WI, USA
- Computational Studies: B_{12} Cofactors and Their Interaction with Enzyme Active Sites

Maurizio Bruschi
University of Milano-Bicocca, Milano, Italy
- Hydrogenases: Theoretical Investigations Towards Bioinspired H_2 Production and Activation

Y. Bu
Shandong University, Jinan, China
- Computational Studies: Proton/Water Coupling to Metals in Biological Reaction Mechanisms

Michael Bühl
University of St. Andrews, Scotland, UK
- Nuclear Magnetic Resonance (NMR) Parameters of Transition Metal Complexes: Methods and Applications

Kieron Burke
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- Approximate Density Functionals: Which Should I Choose?

X. Cao
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- Computational Methods: Lanthanides and Actinides

David A. Case
Rutgers University, Piscataway, NJ, USA
- Broken Symmetry States of Iron–Sulfur Clusters

Jeanet Conradie
University of Tromsø, Tromsø, Norway and University of the Free State, Bloemfontein, South Africa
- Electronic Structure Calculations: Transition Metal–NO Complexes

Nathan R. M. Crawford
University of California, Irvine, CA, USA
- Approximate Density Functionals: Which Should I Choose?

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- Computational Studies: Proton/Water Coupling to Metals in Biological Reaction Mechanisms

Chantal Daniel	*CNRS/Université Louis Pasteur, Strasbourg, France* • Electronic Structure Calculations: Metal Carbonyls
Robert J. Deeth	*University of Warwick, Coventry, UK* • Molecular Mechanics in Bioinorganic Chemistry
Luca De Gioia	*University of Milano-Bicocca, Milano, Italy* • Hydrogenases: Theoretical Investigations Towards Bioinspired H_2 Production and Activation
David A. Dixon	*University of Alabama, Tuscaloosa, AL, USA* • Noble Gas Compounds: Reliable Computational Methods
M. Dolg	*Universität zu Köln, Köln, Germany* • Computational Methods: Lanthanides and Actinides
Piercarlo Fantucci	*University of Milano-Bicocca, Milano, Italy* • Hydrogenases: Theoretical Investigations Towards Bioinspired H_2 Production and Activation
Gernot Frenking	*Philipps-Universität Marburg, Marburg, Germany* • Calculation of Bonding Properties
Richard A. Friesner	*Columbia University, New York, NY, USA* • Modeling Metalloenzymes with Density Functional and Mixed Quantum Mechanical/Molecular Mechanical (QM/MM) Calculations: Progress and Challenges
Filipp Furche	*University of California, Irvine, CA, USA* • Approximate Density Functionals: Which Should I Choose?
Régis Gautier	*Ecole Nationale Supérieure de Chimie de Rennes, Rennes, France* • Computational Methods: Transition Metal Clusters
Abhik Ghosh	*University of Tromsø, Tromsø, Norway* • Electronic Structure Calculations: Transition Metal–NO Complexes
Serge I. Gorelsky	*University of Ottawa, Ottawa, Ontario, Canada* • Ab initio and Semiempirical Methods
Claudio Greco	*University of Milano-Bicocca, Milano, Italy* • Hydrogenases: Theoretical Investigations Towards Bioinspired H_2 Production and Activation
Abebe Habtegabre	*University of New Mexico, Albuquerque, NM, USA* • Reaction Coordinate of Pyranopterin Molybdenum Enzymes
Jean-François Halet	*Ecole Nationale Supérieure de Chimie de Rennes, Rennes, France* • Computational Methods: Transition Metal Clusters
Jeremy N. Harvey	*University of Bristol, Bristol, UK* • Computational Methods: Modeling of Reactivity in Zn-Containing Enzymes
Rosalie K. Hocking	*Stanford University, Stanford, CA, USA and Monash University, Clayton, Australia* • Nature of the Catecholate–Fe(III) Bond: High Affinity Binding and Substrate Activation in Bioinorganic Chemistry
Kathrin H. Hopmann	*University of Tromsø, Tromsø, Norway* • Electronic Structure Calculations: Transition Metal–NO Complexes
Hrant P. Hratchian	*Gaussian Inc., Wallingford, CT, USA* • Spin Contamination in Inorganic Chemistry Calculations

Eluvathingal D. Jemmis	*Indian Institute of Science Education and Research, Thiruvananthapuram, India* • Computational Studies: Boranes
Jan H. Jensen	*University of Copenhagen, Copenhagen, Denmark* • Calculation of Reduction Potential and pK_a
Kasper P. Jensen	*Technical University of Denmark, Lyngby, Denmark* • Computational Studies: Chemical Evolution of Metal Sites
Nikolas Kaltsoyannis	*University College London, London, UK* • Spin-Orbit Coupling: Effects in Heavy Element Chemistry
Martin Kaupp	*University of Würzburg, Würzburg, Germany* • Nuclear Magnetic Resonance (NMR) Parameters of Transition Metal Complexes: Methods and Applications
R. Bruce King	*University of Georgia, Athens, GA, USA* • Theoretical Aspects of Main Group Multiple Bonded Systems
Martin L. Kirk	*University of New Mexico, Albuquerque, NM, USA* • Reaction Coordinate of Pyranopterin Molybdenum Enzymes
Sushilla Knottenbelt	*University of New Mexico, Albuquerque, NM, USA* • Reaction Coordinate of Pyranopterin Molybdenum Enzymes
Nicolai Lehnert	*University of Michigan, Ann Arbor, MI, USA* • Quantum-Chemistry-Centered Normal Coordinate Analysis (QCC-NCA): Application of NCA for the Simulation of the Vibrational Spectra of Large Molecules
Hui Li	*University of Nebraska-Lincoln, Lincoln, NE, USA* • Calculation of Reduction Potential and pK_a
Xavier López	*Universitat Rovira i Virgili, Tarragona, Spain* • Computational Methods: Heteropolyoxoanions
Marcus Lundberg	*Kyoto University, Kyoto, Japan* • Determining Transition States in Bioinorganic Reactions
Yogita Mantri	*Indiana University, Bloomington, IN, USA* • Computational Studies: Cisplatin
Tiziana Marino	*Università della Calabria, Rende, Italy* • Potential Energy Surfaces for Metal-Assisted Chemical Reactions
John E. McGrady	*University of Glasgow, Glasgow, UK* • Electronic Structure of Metal–Metal Bonds
Maria del Carmen Michelini	*Università della Calabria, Rende, Italy* • Potential Energy Surfaces for Metal-Assisted Chemical Reactions
Keiji Morokuma	*Emory University, Atlanta, GA, USA and Kyoto University, Kyoto, Japan* • Determining Transition States in Bioinorganic Reactions
Jon I. Mujika	*University of Bristol, Bristol, UK* • Computational Methods: Modeling of Reactivity in Zn-Containing Enzymes
Adrian J. Mulholland	*University of Bristol, Bristol, UK* • Computational Methods: Modeling of Reactivity in Zn-Containing Enzymes

Frank Neese	*University of Bonn, Bonn, Germany and Max-Planck Institute for Bioinorganic Chemistry, Mülheim, Germany* • Spectroscopic Properties of Protein-Bound Cofactors: Calculation by Combined Quantum Mechanical/Molecular Mechanical (QM/MM) Approaches
Gabriela Nemeş	*Babeş-Bolyai University, Cluj-Napoca, Romania* • Theoretical Aspects of Main Group Multiple Bonded Systems
Louis Noodleman	*Scripps Research Institute, La Jolla, CA, USA* • Broken Symmetry States of Iron–Sulfur Clusters
Maylis Orio	*University of Bonn, Bonn, Germany* • Spectroscopic Properties of Protein-Bound Cofactors: Calculation by Combined Quantum Mechanical/Molecular Mechanical (QM/MM) Approaches
Monita Y. M. Pau	*Stanford University, Stanford, CA, USA* • Nature of the Catecholate–Fe(III) Bond: High Affinity Binding and Substrate Activation in Bioinorganic Chemistry
Kirk A. Peterson	*Washington State University, Pullman, WA, USA* • Gaussian Basis Sets for Quantum Mechanical (QM) Calculations
Petronela Petrar	*Babeş-Bolyai University, Cluj-Napoca, Romania* • Theoretical Aspects of Main Group Multiple Bonded Systems
Josep M. Poblet	*Universitat Rovira i Virgili, Tarragona, Spain* • Computational Methods: Heteropolyoxoanions
Dragan M. Popović	*University of California, Davis, CA, USA* • Combined Density Functional Theory (DFT) and Electrostatics Study of the Proton Pumping Mechanism in Cytochrome *c* Oxidase
Jason Quenneville	*University of California, Davis, CA, USA* • Combined Density Functional Theory (DFT) and Electrostatics Study of the Proton Pumping Mechanism in Cytochrome *c* Oxidase
Dmitrij Rappoport	*University of California, Irvine, CA, USA* • Approximate Density Functionals: Which Should I Choose?
Christoph Riplinger	*University of Bonn, Bonn, Germany* • Spectroscopic Properties of Protein-Bound Cofactors: Calculation by Combined Quantum Mechanical/Molecular Mechanical (QM/MM) Approaches
Björn O. Roos	*Chemical Center, Lund, Sweden* • Multiconfigurational Quantum Mechanics (QM) for Heavy Element Compounds
Nino Russo	*Università della Calabria, Rende, Italy* • Potential Energy Surfaces for Metal-Assisted Chemical Reactions
Ulf Ryde	*Lund University, Lund, Sweden* • Quantum Mechanical/Molecular Mechanical (QM/MM) Methods and Applications in Bioinorganic Chemistry
Jean-Yves Saillard	*Ecole Nationale Supérieure de Chimie de Rennes, Rennes, France* • Computational Methods: Transition Metal Clusters
H. Bernhard Schlegel	*Wayne State University, Detroit, MI, USA* • Spin Contamination in Inorganic Chemistry Calculations

Oottikkal Shameema
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Emilia Sicilia
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- Potential Energy Surfaces for Metal-Assisted Chemical Reactions

Per E. M. Siegbahn
Stockholm University, Stockholm, Sweden
- Water Oxidation by the Manganese Cluster in Photosynthesis

Ioan Silaghi-Dumitrescu
Babeş-Bolyai University, Cluj-Napoca, Romania
- Theoretical Aspects of Main Group Multiple Bonded Systems

Edward I. Solomon
Stanford University, Stanford, CA, USA
- Nature of the Catecholate–Fe(III) Bond: High Affinity Binding and Substrate Activation in Bioinorganic Chemistry

Jason L. Sonnenberg
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- Spin Contamination in Inorganic Chemistry Calculations

Alexei A. Stuchebrukhov
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- Combined Density Functional Theory (DFT) and Electrostatics Study of the Proton Pumping Mechanism in Cytochrome *c* Oxidase

Mahesh Sundararajan
University of Bonn, Bonn, Germany
- Spectroscopic Properties of Protein-Bound Cofactors: Calculation by Combined Quantum Mechanical/Molecular Mechanical (QM/MM) Approaches

Robert K. Szilagyi
Montana State University, Bozeman, MT, USA
- Structural Origins of Noninnocent Coordination Chemistry

Marirosa Toscano
Università della Calabria, Rende, Italy
- Potential Energy Surfaces for Metal-Assisted Chemical Reactions

Felix Tuczek
Christian-Albrechts-Universität Kiel, Kiel, Germany
- Electronic Structure Calculations: Dinitrogen Reduction in Nitrogenase and Synthetic Model Systems

Moritz von Hopffgarten
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- Calculation of Bonding Properties

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- Spectroscopic Properties of Protein-Bound Cofactors: Calculation by Combined Quantum Mechanical/Molecular Mechanical (QM/MM) Approaches

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- Hydrogenases: Theoretical Investigations Towards Bioinspired H_2 Production and Activation

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- Multiple Aromaticity, Multiple Antiaromaticity, and Conflicting Aromaticity in Inorganic Systems

Series Preface

The success of the *Encyclopedia of Inorganic Chemistry* (EIC) has been very gratifying to the Editors. We felt, however, that not everyone would necessarily need access to the full ten volumes of EIC. Some readers might prefer to have more concise thematic volumes targeted to their specific area of interest. This idea encouraged us to produce a series of EIC Books, focusing on topics of current interest. These books will continue to appear on a regular basis and will feature leading scholars in their fields. Like the Encyclopedia, we hope that EIC Books will give both the starting research student and the confirmed research worker a critical distillation of the leading concepts and provide a structured entry into the fields covered.

Computer literature searches have become so easy that one could be led into thinking that the problem of efficient access to chemical knowledge is now solved. In fact, these searches often produce such a vast mass of material that the reader is overwhelmed. As Henry Kissinger has remarked, the end result is often a shrinking of one's perspective. From studying the volumes that comprise the EIC Books series, we hope that readers will find an expanding perspective to furnish ideas for research, and a solid, up-to-date digest of current knowledge to provide a basis for instructors and lecturers.

I take this opportunity of thanking Bruce King, who pioneered the *Encyclopedia of Inorganic Chemistry*, my fellow editors, as well as the Wiley personnel, and, most particularly, the authors of the articles for the tremendous effort required to produce such a series on time. I hope that EIC Books will allow readers to benefit in a more timely way from the insight of the authors and thus contribute to the advance of the field as a whole.

Robert H. Crabtree
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January 2009

Volume Preface

Over the past several decades there have been major advances in our ability to evaluate computationally the electronic structure of inorganic molecules, particularly transition metal systems. This is due to the Moore's Law increase in computing power as well as the impact of density functional theory (DFT) and its implementation in commercial and freeware programs for quantum chemical calculations. Improved pure and hybrid density functionals are now allowing DFT calculations with accuracy comparable to high level Hartree–Fock (HF) treatments, and the results of these calculations can now be evaluated based on experiment. The latter is made possible through the development of modules for the calculation of spin-Hamiltonian parameters and other ground state properties (vibrational frequencies, g and A matrices, D tensor, etc.) and ΔSCF and time-dependent density functional theory (TDDFT) methods for correlation to electronic excited states. Developments in wave function methods have also extended their use to a wide range of transition metal systems.

The availability and ease in utility of electronic structure codes have led to their becoming a significant component of the experimental chemist's toolbox. Indeed many papers on inorganic systems in the major chemical literature now contain electronic structure calculations as a complement to experimental results. Despite the significant advances in theory, the accuracy of computational methods is still limited when applied to transition metal systems, and different DFT functionals, levels of implementation of HF based methods (Moeller-Plesset perturbation theory (MP), complete active space (CAS), coupled cluster (CC), configurational interaction (CI)), and model designs can give different results. It is therefore of critical importance to calibrate calculations with experiments. However, when calculations are correlated to and supported by experimental data they can provide fundamental insight into electronic structure and its contributions to physical properties and chemical reactivity. This interplay will continue to expand and contribute to both improved value of experimental results and improved accuracy of computational predictions.

The purpose of this volume is to provide state-of-the-art presentations of quantum mechanical and related methods and their applications by many of the leaders in the field. Part 1 of this volume focuses on methods, their background and implementation, and their use in describing bonding properties, energies, transition states and spectroscopic features. Then we focus on applications in bioinorganic chemistry (Part 2) and inorganic chemistry (Part 3) where electronic structure calculations have already had a major impact. We believe this volume will be of significant value to both experimentalists and theoreticians, and anticipate that it will stimulate both further development of the methodology and its applications in the many interdisciplinary fields that comprise modern inorganic chemistry.

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September 2009

PART 1

Methods

Calculation of Bonding Properties

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1 INTRODUCTION

The description of chemical bonding with heuristic bonding models is an essential part of chemical research since the early days of chemistry.[1] Chemists use a particular language and special symbols that convey information about the bonding properties of molecules, which is useful for chemical research in order to explain their structure and reactivity. The development of quantum chemistry during the last decades[2] has led to a situation where the accuracy of the calculated geometries, energies, spectroscopic data, and other properties may now challenge experimental values. Quantum chemical methods have also been used to analyze the bonding situation in molecules and solids aiming at a qualitative understanding of the nature of the chemical bond.[3,4] Numerous charge and energy partitioning techniques were developed which establish a bridge between the prequantum theoretical heuristic bonding models and the numerical results of quantum chemical calculations. The former models were derived and further refined in a neural network of experimental observations, which helped to establish a classification system for the enormous diversity of chemical phenomena. A litmus test for the usefulness of heuristic ad hoc models and for the quantum chemically derived bonding models are new molecules which exhibit hitherto unknown structural motifs and/or reactivities. A pertinent historical example is pericyclic reactions that could only be explained with the introduction of the frontier orbital model of Fukui[5,6] and the orbital symmetry model of Woodward and Hoffmann.[7]

Inorganic compounds show a much greater variety in structural motifs and bonding properties than organic compounds because of the significantly larger number of elements that are considered. In the following, we provide examples that show that quantum chemical bonding models, which are based on unambigously defined theoretical terms, can be very useful to examine and to complement heuristic concepts of chemical bonding. The advantage of the former approaches comes from the numerical values, which can be used to estimate the well-defined terms of the interatomic interactions. Two examples from main group chemistry and two examples for transition-metal complexes were chosen. The main group compounds are the apparently trivial and well-understood diatomic molecules H_2, N_2, CO, BF, and the recently synthesized heavy-atom group-14 homologs of alkynes REER ($E = Si$–Pb) whose bonding situation has been a topic of controversies. The discussion of the nature of the chemical bonds in the main group compounds aims at connecting the description in terms of classical Lewis structures with an energy decomposition analysis of the calculated electronic structures.

We also discuss the chemical bonds in transition metal carbonyl complexes that are archetypical parent

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compounds for transition metals. The second transition-metal topic focuses on the bonding situation in the recently synthesized molybdenum compound $[Mo(ZnMe)_9(ZnCp^*)_3]$, which has the coordination number 12. In the discussion of the transition-metal compounds, we compare the Dewar–Chatt–Duncanson (DCD) model with the bonding analysis using quantum chemical calculations.

The bonding properties of the molecules have been calculated and analyzed with the energy decomposition analysis (EDA), which was introduced more than 30 years ago by Ziegler and Rauk and by Morokuma. The next section gives a short account of the EDA. A more detailed discussion can be found in the literature.[8–12]

2 EDA METHOD

It seems obvious to use the experimental value of the bond dissociation energy (BDE) D_e to estimate the strength of a chemical bond A–B between the fragments A and B. The use of the D_e values for analyzing the nature of the bond A–B may be misleading, however, because the BDE refers to the energy difference between AB and the fragments A and B at the respective equilibrium geometry and in their electronic ground states. It is more reasonable for analyzing the chemical bond to use the instantaneous interaction energy, ΔE_{int}, of the bond A–B, which is the calculated energy difference between the molecule and the fragments in the frozen geometry of the compound.

$$-D_e = \Delta E = \Delta E_{\text{int}} + \Delta E_{\text{prep}} \qquad (1)$$

The EDA takes the calculated ΔE_{int} values as the starting point for the bonding analysis. The interaction energy is divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \qquad (2)$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments, which are calculated using the frozen electron density distribution of the fragments in the geometry of the molecules and in the electronic reference state, which may or may not be the electronic ground state. The second term in equation (2), ΔE_{Pauli}, refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. ΔE_{Pauli} is calculated by enforcing the Kohn–Sham determinant on the superimposed fragments to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the energy partitioning analysis when the Kohn–Sham orbitals relax to their optimal form. This term can be further partitioned into contributions by the orbitals belonging to different irreducible representations of the point group of the interacting system.

3 DIATOMIC MOLECULES H_2, N_2, CO, BF

The EDA results for the chemical bond in H_2 provide quantitative support for the suggestion that the binding interactions come solely from orbital interactions. Table 1 shows that ΔE_{orb} is the only attractive term that contributes to the H–H bond while the electrostatic term at the equilibrium distance is slightly repulsive. The ΔE_{elstat} term becomes weakly attractive at longer distances but the energy minimum is very shallow (~10 kcal mol^{-1}) at r(H–H) ~0.9 Å, which is significantly longer than the equilibrium value (0.745 Å). There is no Pauli repulsion in H_2 because there are only two electrons with opposite spins. Note that the BDE of the diatomic species H_2, N_2, CO, BF is the same as the interaction energy ΔE_{int} because there is no preparation energy ΔE_{prep}.

The EDA results for N_2 exhibit a significantly different picture. There is a very strong Pauli repulsion

Table 1 Energy decomposition analysis of the H–H, N–N, C–O, and B–F bonds at RPBE/TZP.[(a)] Energy values in kilocalories per mole. Bond lengths R in angstrom. Experimental values are given in parentheses

	H_2	N_2	CO	BF
ΔE_{int}	−112.9	−232.2	−258.4	−180.8
ΔE_{Pauli}	0.0	791.7	575.8	476.1
$\Delta E_{\text{elstat}}{}^{(b)}$	+5.8	−308.5 (30.1%)	−240.0 (28.8%)	−210.5 (32.0%)
$\Delta E_{\text{orb}}{}^{(b)}$	−118.7 (100%)	−715.4 (69.9%)	−594.2 (71.2%)	−446.4 (68.0%)
$\Delta E_{\sigma}{}^{(c)}$	−118.7 (100%)	−470.0 (65.7%)	−301.7 (50.8%)	−396.4 (88.8%)
$\Delta E_{\pi}{}^{(c)}$	0.0	−245.4 (34.3%)	−292.5 (49.2%)	−50.0 (11.2%)
R	0.745 (0.741)	1.105 (1.09768)	1.144 (1.128)	1.285 (1.262)
D_e	−112.9	−232.2	−258.4	−180.8
D_o	−106.3 (−103.3)	−228.8 (−225.0)	−255.4 (−255.7)	−178.9 (179.9)

(a) Ref. 13.
(b) The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$.
(c) The values in parentheses give the percentage contribution to the orbital interactions ΔE_{orb}.

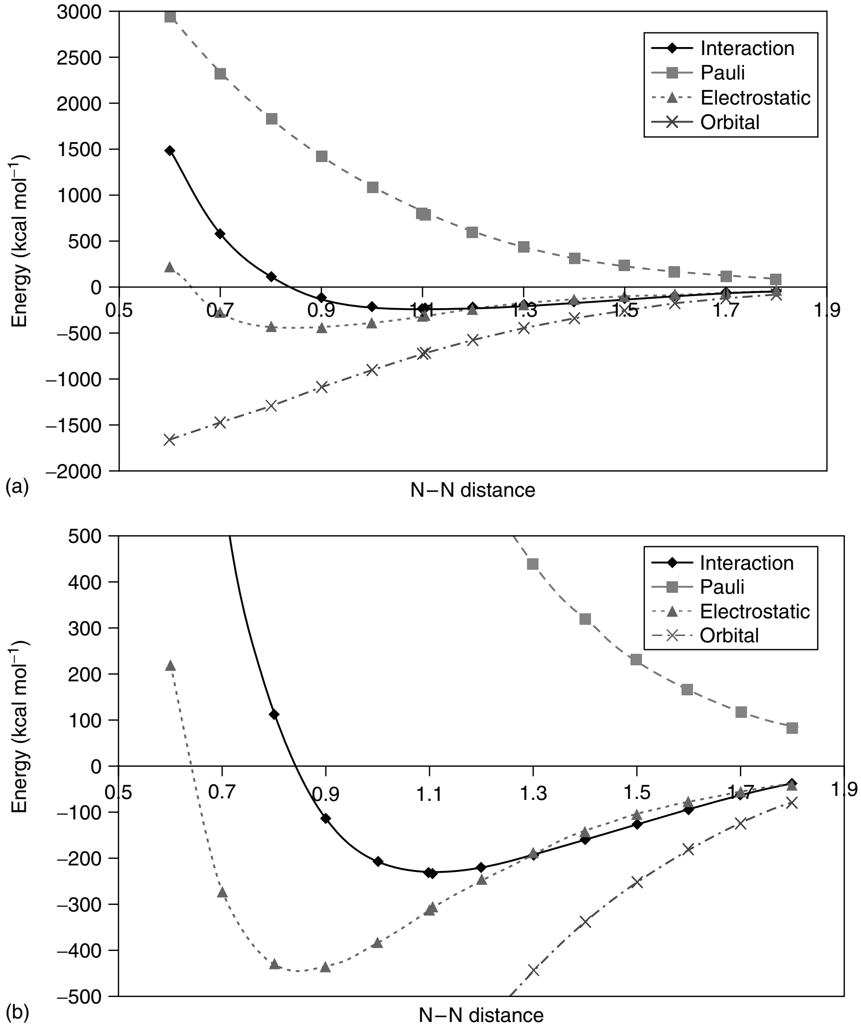


Figure 1 Energy contributions to the bonding in N_2 as a function of N–N interatomic distance (angstrom) calculated at RPBE/TZP. (a) Small scale and (b) large scale

of $\Delta E_{\mathrm{Pauli}} = 791.7\,\mathrm{kcal\,mol^{-1}}$, which compensates for the attractive orbital interactions $\Delta E_{\mathrm{orb}} = -715.4\,\mathrm{kcal\,mol^{-1}}$. The latter term can be divided into $-470.0\,\mathrm{kcal\,mol^{-1}}$ (65.7%) which come from the σ orbitals and $-245.4\,\mathrm{kcal\,mol^{-1}}$ (34.3%), which come from the π orbitals. Surprisingly, the contribution of the electrostatic interactions $\Delta E_{\mathrm{elstat}} = -308.5\,\mathrm{kcal\,mol^{-1}}$ is strongly attractive. Figure 1 shows a plot of the energy terms at different N–N distances. It becomes obvious that ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$ become even more strongly attractive at shorter distances than the equilibrium value. The shortening is prevented by the steep increase of the Pauli repulsion. The energy curves for N_2 are typical for the chemical bond of bonded atoms that are heavier than hydrogen. The chemical bond in H_2 is atypical because (i) there is no Pauli repulsion and (ii) there is only weak electrostatic attraction because of the small charge of the light atomic nuclei.

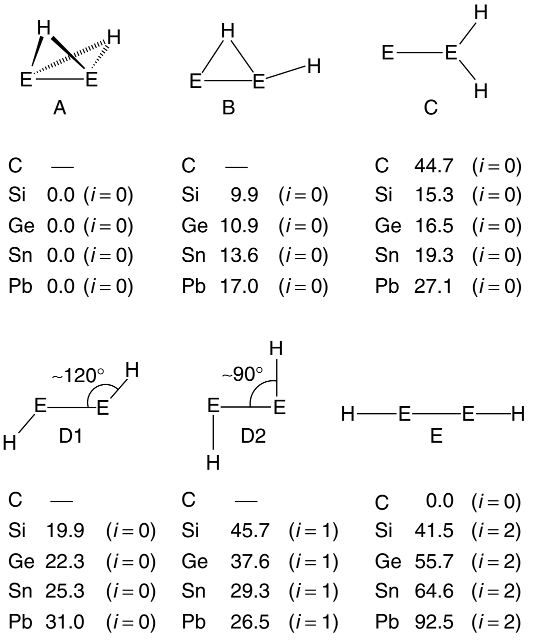
Table 1 shows that the BDE of CO is higher ($258.4\,\mathrm{kcal\,mol^{-1}}$) than for N_2 ($232.2\,\mathrm{kcal\,mol^{-1}}$). Inspection of the energy terms reveals that the stronger C–O bond does not come from stronger attraction but from weaker Pauli repulsion than in N_2. The ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$ values for CO are smaller than for N_2 but the weaker attraction is overcompensated by the much smaller $\Delta E_{\mathrm{Pauli}}$ value. The EDA results also show that the relative contribution of the π orbitals to the ΔE_{orb} term in CO (49.2%) is higher than in N_2 (34.3%). The molecule BF is isoelectronic with N_2 and CO but it has the lowest bond dissociation energy of the three species (Table 1). The Pauli repulsion in BF is still smaller than in CO but it does not compensate for the loss of the attractive contributions of ΔE_{orb} and $\Delta E_{\mathrm{elstat}}$. On closer examination, it becomes obvious that there is a particularly weak contribution of the π orbitals in BF, which comprise only 11.2% of ΔE_{orb}. The latter result is in agreement with the Lewis bonding model for BF, which is usually written with a single bond, not with a triple bond. The EDA results thus suggest that the stronger bond of CO compared with N_2 comes from the weaker Pauli repulsion in the former compound while the weaker bond in BF is explained by the dramatic loss of π bonding.

4 ACETYLENE AND HEAVIER GROUP-14 HOMOLOGS HEEH (E = C–Pb)

Chemical experience shows that molecules, which have multiple bonds between heavier atoms than those of the first octal row, are much less stable and are more difficult to synthesize than the homologs of the lighter atoms. This holds, in particular, for the heavier group-14 homologs of alkynes RC≡CR. It was only in the years 2000 until 2004 that compounds REER where E = Si, Ge, Sn, Pb with bulky substituents R could be synthesized and isolated for X-ray structure analysis.[14,15,16] Unlike acetylene and alkynes, which have a linear RCCR geometry, the heavier group-14 compounds REER all have a strongly trans-bent structure where the angle $\tau(\text{REE}) = 120-125°$ for E = Si, Ge, Sn, and $\tau(\text{REE}) = \sim 96°$ for E = Pb. There has been much debate if the E–E bond in the trans-bent structures of REER should be considered a triple bond.

A straightforward answer to the question about the nature of the E–E bond in REER can be given when the equilibrium structures of the parent systems HEEH are analyzed with quantum chemical methods. Figure 2 shows six different stationary points, which are found on the singlet potential energy surface (PES) of E_2H_2. It becomes clear that the heavier atoms exhibit vastly different structural motifs than carbon. The only energy minima for carbon are the acetylene form **E** and the energetically much higher lying vinylidene isomer **C**. The global energy minimum for the heavier group-14 atoms Si–Pb is the doubly hydrogen-bridged butterfly structure **A**. The next higher lying form of the latter elements is the planar singly hydrogen-bridged isomer **B**, which has a very unusual geometry. Structures **A** and **B** of E_2H_2 have been isolated for E = Si, Ge in a low-temperature matrix and they were identified through comparison of their experimental vibrational spectra with calculated values. The vinylidene form **C** and the trans-bent form **D1** are for all heavy elements slightly less stable than **B**. There is another trans-bent form **D2** (Figure 2) with a more acute bonding angle $\tau(\text{HEE}) = \sim 90°$ which for E = Pb is even lower in energy than **D1** but the former species is a transition state for the degenerate wing flapping isomerization of **A**. The linear form **E** of the heavier group-14 atoms is an energetically high-lying second-order saddle point. Bulky substituents in REER make the isomers **A** and **B** less stable than the trans-bent structures **D1** and **D2**, which explains why only the latter could become isolated at room temperature when *R* is very big.

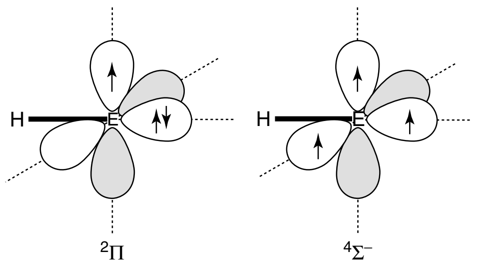
The unusual geometries of **A, B, D1**, and **D2** are difficult to explain with Lewis structures but their appearance is easily understood when the electronic structure of the fragments EH is considered.[16] We do not discuss the vinylidene structure **C** because it has a different connectivity than the other isomers. Figure 3 schematically shows the $X^2\Pi$ ground state and the $a^4\Sigma^-$ first excited state of EH. It becomes obvious that the latter electronic state is the proper reference state for the acetylene-like structure because it has one unpaired electron in a σ orbital and two electrons in a degenerate π orbital. This means that the EH fragments must first become excited into the $a^4\Sigma^-$ state in order to bind through a σ and degenerate π bond in



	A	B	C
C	—	—	44.7 ($i = 0$)
Si	0.0 ($i = 0$)	9.9 ($i = 0$)	15.3 ($i = 0$)
Ge	0.0 ($i = 0$)	10.9 ($i = 0$)	16.5 ($i = 0$)
Sn	0.0 ($i = 0$)	13.6 ($i = 0$)	19.3 ($i = 0$)
Pb	0.0 ($i = 0$)	17.0 ($i = 0$)	27.1 ($i = 0$)

	D1	D2	E
C	—	—	0.0 ($i = 0$)
Si	19.9 ($i = 0$)	45.7 ($i = 1$)	41.5 ($i = 2$)
Ge	22.3 ($i = 0$)	37.6 ($i = 1$)	55.7 ($i = 2$)
Sn	25.3 ($i = 0$)	29.3 ($i = 1$)	64.6 ($i = 2$)
Pb	31.0 ($i = 0$)	26.5 ($i = 1$)	92.5 ($i = 2$)

Figure 2 Schematic representation of the E_2H_2 isomers. Relative energies (kilocalories per mole) at BP86/QZ4P and number of imaginary frequencies *i*



$^2\Pi$	$^4\Sigma^-$ Exp.	Calc.	
0.0	16.7	15.4	(E=C)
	36.4	38.6	(E=Si)
	47.8	47.1	(E=Ge)
	44.5	45.9	(E=Sn)
	50.3	52.0	(E=Pb)

Figure 3 Schematic representation of the electron configuration of the $^2\Pi$ electronic ground state and the $a^4\Sigma^-$ excited state of EH (E = C–Pb). Experimental and calculated (BP86/QZ4P) excitation energies are given as (kilocalories per mole)

Table 2 Calculated bond dissociation energies D_e (kilocalories per mole) of linear HE≡EH $\rightarrow$ 2 EH ($a^4\Sigma^-$) and $X^2\Pi \rightarrow a^4\Sigma^-$ excitation energies ΔE_{exc} (kilocalories per mole) of EH at BP86/QZ4P

E	D_e	ΔE_{exc}	$D_e - 2x\Delta E_{exc}$
C	270.9	15.44	240.0
Si	121.6	38.56	44.5
Ge	113.3	47.09	19.0
Sn	89.4	45.87	−2.3
Pb	69.0	52.01	−35.0

HE≡EH (**E**). The electron configuration of the $^2\Pi$ ground state allows only one electron-sharing single bond between two EH moieties. Figure 3 shows that CH has the lowest $X^2\Pi \rightarrow a^4\Sigma^-$ excitation energy while the heavier homologs need much more energy to reach the $a^4\Sigma^-$ excited state. It means that CH requires much less excitation energy in order to form a triple bond than the heavier EH species.

Table 2 gives the calculated bond dissociation energies of linear HE≡EH species for E = C–Pb and the excitation energies $2x\Delta E_{exc}$, which is the energy penalty that must be paid by the fragments in order to allow for the formation of a triple bond. The very high BDE of $D_e = 270.7\,\text{kcal mol}^{-1}$ for the carbon species indicates a substantial energy gain of $240.0\,\text{kcal mol}^{-1}$ for acetylene, which shows that it is energetically profitable for the CH fragments to form a HC≡CH triple bond through the $a^4\Sigma^-$ excited state. A C–C single bond that can be formed from the $X^2\Pi$ ground state would deliver much less binding energy. Typical C–C single bonds have bond energies of only $80-90\,\text{kcal mol}^{-1}$. The situation is very different for the heavier homologs SiH–PbH. The calculations predict that the hypothetical linear molecule HSi≡SiH would have a bond dissociation energy for breaking the triple bond of $D_e = 121.6\,\text{kcal mol}^{-1}$, which is much less than for acetylene. The $X^2\Pi \rightarrow a^4\Sigma^-$ excitation energy for the SiH fragments is $2x\Delta E_{exc} = 77.1\,\text{kcal mol}^{-1}$, which is much higher than for CH (Table 2). Thus, the gain in the binding energy for the silicon system is only $D_e - 2x\Delta E_{exc} = 44.5\,\text{kcal mol}^{-1}$. This is much less than the stabilization energy that can be expected from the formation of an electron-sharing HSi–SiH single bond between two SiH moieties in the $X^2\Pi$ ground state. Typical bond dissociation energies of Si–Si single bonds are $75-80\,\text{kcal mol}^{-1}$. Thus, it is energetically more profitable for two SiH species to bind through their $X^2\Pi$ ground state than through the $a^4\Sigma^-$ excited state. This holds even more for the heavier homologs GeH–PbH. Table 2 shows that the additional binding energy of the latter diatomics in the linear structure HE≡EH is only $19.0\,\text{kcal mol}^{-1}$ for E = Ge while the excitation energies of two EH fragments where E = Sn, Pb are even higher than the bond dissociation energy of linear HE≡EH.

The formation of the unusual structures **A, B, D1**, and **D2** can now easily be explained when the interacting

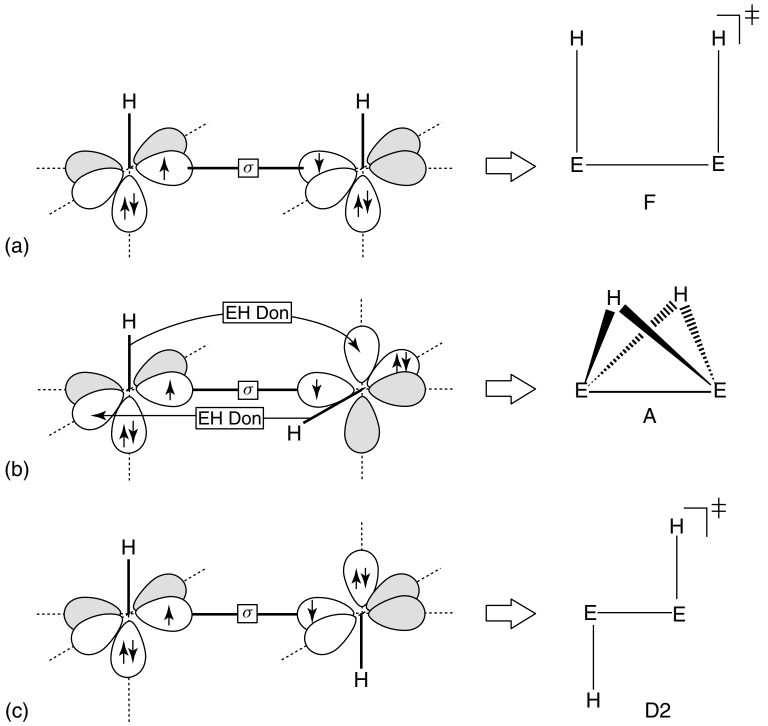


Figure 4 Qualitative model for the orbital interactions between two EH molecules in different orientations where the unpaired electrons yield a σ bond

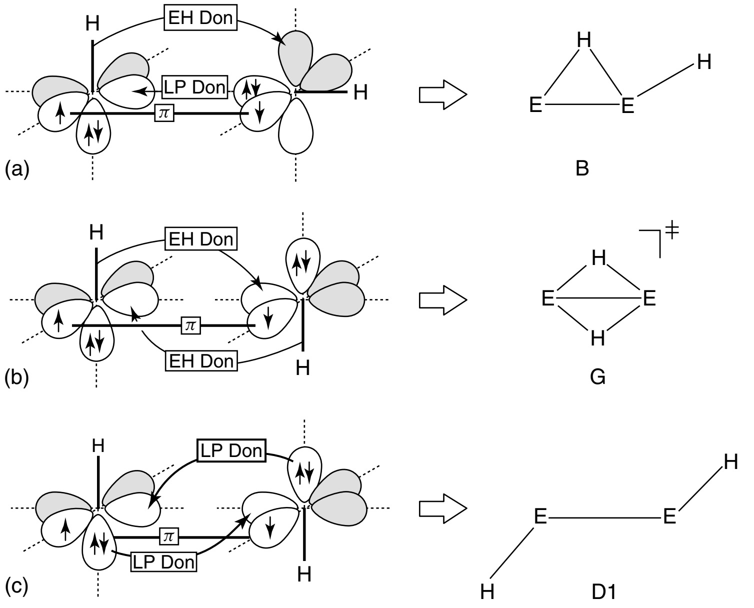


Figure 5 Qualitative model for the orbital interactions between two EH molecules in different orientations where the unpaired electrons yield a π bond

fragments EH in the $X^2\Pi$ ground state are used as building blocks. Figure 4 schematically shows the arrangement of the EH fragments where the unpaired electrons yield a σ bond. There are several conformations for rotation about the σ bond. The C–H bonds and the lone-pair (lp) orbitals of the fragments are eclipsed in the syn–planar arrangement leading to **F** (Figure 4a), which is energetically unfavorable because the vacant $p(\pi)$ orbitals remain unoccupied while the E–H bonds and the electron lps of the two molecules repel each other. The geometry optimization of **F** under C_{2v} symmetry constraint gives a structure, which is the transition state for degenerate rearrangement of the global energy minimum **A**. The latter form is obtained from **F** through rotation about the σ-bond axis by 90°, which gives a much more favorable arrangement (Figure 4b). The empty $p(\pi)$ orbitals of EH can now interact in E_2H_2 with the E–H bond and with the electron lp of the other EH. Note that the E–H bonds are better donors than the electron lps for heavier elements E because the lp orbitals have mainly s-character and because hydrogen is more electronegative than Si–Pb. The E–H bonds are tilted toward the empty $p(\pi)$ orbitals of the other EH moiety in order to enhance the donor–acceptor interactions, which directly leads to the doubly bridged butterfly structure **A**. Note that there are three bonding components of the orbital interactions in **A**, one σ bond and two (degenerate) E–H donor–acceptor bonds.

Figure 4c shows the antiplanar arrangement of the EH fragments yielding the structure **D2** whose E–E bonding contribution comes only from the σ orbital between the atoms E. The structure **D2** lacks the two EH donor–acceptor interactions of **A**. The former isomer may become lower in energy than the latter if the hydrogen atoms are substituted by bulky groups such as the terphenyl substituent, which was used in the synthesis of the R^*PbPbR^* compound.

Rather than a σ bond, the unpaired electrons in the $X^2\Pi$ ground state of EH may alternatively yield an electron-sharing bond of $(EH)_2$, which possesses π symmetry with respect to the molecular structure. Figure 5 shows three different orientations for the $(X^2\Pi)$ EH molecules, which lead to an E–E π bond. The arrangement, which is given in Figure 5(a), that leads to structure **B** has an electron lp of one EH moiety pointing in the direction of the empty p orbital of the other EH species. This orbital interaction now has σ symmetry with respect to the $(EH)_2$ dimer. Besides the electron-sharing π bond and the lp donor–acceptor σ bond, further stabilizing orbital interactions come from the donation of the EH bonding orbital and possibly the electron lp of that EH molecule, which serves as the lp σ acceptor (bottom EH in Figure 5a) into the empty p orbital of the lp donor EH (top EH in Figure 5a). As noted before, donation from the EH bonding orbital is stronger than from the lp orbital. The former interaction becomes stronger when the EH donor orbital and the empty p orbital of the interacting fragments are tilted toward each other, which leads to structure **B**. The tilting of the empty p orbital of the acceptor EH moiety (top EH in Figure 5a) means that the terminal hydrogen atom moves toward the bridging hydrogen atom. The syn orientation of the terminal hydrogen atom with respect to the bridging H atom can be explained as a secondary effect of optimizing the EH donor–acceptor interaction, which is shown in Figure 5(a). The unusual singly bridged geometry of **B**, which has a terminal hydrogen atom with syn orientation to the bridging atom can thus be straightforwardly explained