Exploring the Chemistry of $\lambda^3$-iodanes: The Role of Hypervalent Bonding

Halua Pinto de Magalhães
Exploring the Chemistry of $\lambda^3$-Iodanes:
The Role of Hypervalent Bonding

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by
HALUA PINTO DE MAGALHÃES

Master of Science ETH in Chemistry

born on 28.06.1986

 citizen of Ilanz GR

accepted on the recommendation of

PD Dr. Hans Peter Lüthi, examiner
Prof. Dr. Antonio Togni & Prof. Dr. Jürg Hutter, co-examiners

2015
You have to act as if it were possible to radically transform the world. And you have to do it all the time.

Angela Davis
Acknowledgements

During my studies, I have been supported by many people. Without their help, profound knowledge and creativity, this thesis would not have been possible. Therefore I would like to extend my sincere gratitude to all of them.

First of all, I would like to thank my supervisor, Hans Peter Lüthi. I am very grateful for all the inspiration, critical discussions and patience he showed. Gratitude also for enduring my time consuming political activities, which now and then interfered with the everyday work.

Many thanks go to my co-supervisor Antonio Togni, who opened up the opportunity for this interdisciplinary exchange between computational and synthetic chemistry. His open mind and interest in theory allowed for an application-oriented and successful collaboration.

In addition, I thank my co-examiner Jürg Hutter for his interest in this subject and the effort of reading my thesis in great detail.

I also place on record, my sense of gratitude to Patrick Bultinck for the hosting at his laboratory in Ghent. I have spent a very enriching time in his group which resulted in a fruitful collaboration. The theoretical background of this work has greatly benefited from his contribution.

I would like to express my appreciation to Markus Reiher for the integration in his research group and providing an adequate infrastructure to perform state of the art computational chemistry. The same goes for Wilfred van Gunsteren who hosted our small group till the days of his retirement.

Special acknowledgements to Oliver Sala who supported me scientifically, but even more socially, through this venture. I feel gratitude for Katrin Niedermann
and Nico Santschi for the scientific discussions about the chemistry addressed in this work. Thanks to Stefan Knecht for his assistance in performing the relativistic calculations. I also will not forget all my colleagues in the Reiher group, as well as the former van Gunsteren group. The same goes for the members of the Togni Group who endured several of my computational talks.

The full value of appreciation is dedicated to my mother for her unceasing encouragement, support and attention. The fullest respect also to my closest friends, Fuat, Jan and Ingo, who always got my back. A bunch of props to Kijan for opening whole new perspectives on our society. I am also grateful to Nicole who supported me in past years.

In order to make the most of this opportunity, I wish to express my thanks to one and all who, directly or indirectly, have lent their hand in this venture.

This research was supported by the Swiss National Science Foundation (SNF).
The broad range for the application of hypervalent iodine reagents in organic synthesis continuously popularized their use over the past few years. Much is already known experimentally about the properties and the reactivity of these iodane compounds. In contrast, the contribution of modern electronic structure theory in this area of chemistry has been rather modest so far. Therefore, it is the concern of the presented thesis to explore such $\lambda^3$-iodanes in terms of multi-center bonding and its relevance for the reactivity observed in experiments as well as in silico.

Considerable attention was addressed to the mechanistic diversity, which was investigated in great detail. The quantum chemical calculations revealed that reactive $\lambda^3$-iodane intermediates can operate as “gateway” determining the course and selectivity of the reaction. Such iodine-guided functionalization reactions follow a Curtin-Hammett type reaction profile, with the reductive elimination of the products as the rate determining step. $\lambda^3$-Iodane reaction patterns are accompanied by a remarkable affinity of the hypervalent region to planarity for all reactions observed. This phenomenon is related to a pseudo Jahn-Teller (PJT) effect and is, in fact, also the driving force for the rapid isomerization of these T-shaped iodanes via a Y-shape transition structure. The selectivity of the overall reaction could additionally be related to the polarity of the 3-center-4-electron bond.

In order to aim for a more general understanding of the unusual reactivity of $\lambda^3$-iodanes, a more advanced description of bonding in these compounds was necessary. Multi-center bonding was evaluated by the analysis of Domain Averaged Fermi Holes that allowed the differentiation between features of the electronic structure and to establish a relationship between the occurrence of multi-center bonding and structural parameters. The 3-center-4-electron bond model proved to be explicitly valid for those molecules, which exhibit a coupling
beyond a single electron pair. This was observed for $\lambda^3$-iodanes coordinated by apolar ligands and also results in high reaction barriers for reductive elimination, as well as isomerization reactions. However, compounds carrying electron-withdrawing ligands fall into a different category: the pairing of electrons is restricted to extend over two centers only, thus challenging the 3-center bonding pattern. In the end, this setting provided a sound basis for the investigations of alternative routes of the novel Ritter-type reaction, in which N-trifluoromethyl amides are obtained by electrophilic trifluoromethylation.

Efforts were also directed for the exploration of relativistic effects on hypervalent iodine compounds. Valuable insight into structure and bonding were gained by means of relativistic Projection analysis, which allows evaluation of atomic contributions to the iodine contact density. The importance of incorporating scalar effects into the iodine basis is well-known from a quantum relativistic perspective, yet the impact of spin-orbit coupling on hypervalent bonding appeared to be only marginal.
In den vergangenen Jahren zeichnete sich eine beachtliche Entwicklung im Bereich der hypervalenten Iod-Verbindungen ab, welche sich in ihrem vielfältigen Einsatz als Reagenzien in der organischen Synthese widerspiegelt. Über die Eigenschaften und Reaktivität dieser Verbindungen ist bereits viel bekannt, der Beitrag der modernen Elektronenstruktur-Theorie dazu hält sich allerdings in Grenzen. Die vorliegende Forschungsarbeit dieser Dissertation widmet sich daher der spezifischen Studie über \( \lambda^3 \)-Iodan-Verbindungen und untersucht, welche Rolle dabei multizentrische Bindungen einnehmen.


# Contents

Acknowledgements v
Summary vii
Zusammenfassung ix
Publications xiii

1 Introduction 1
  1.1 Hypervalent Iodine Compounds .......................... 1
  1.2 The Chemistry of $\lambda^3$-Iodanes ....................... 5
  1.3 Outline of the Thesis ................................... 6

2 Methodology and Theoretical Background 9
  2.1 Partitioning of the Electron Density ...................... 10
    2.1.1 Natural Orbital Decomposition .................... 10
  2.2 Domain Averaged Fermi Holes ........................... 12
    2.2.1 Practical Notes on DAFH ........................... 16
    2.2.2 Workflow of the DAFH Analysis .................... 17
  2.3 Projection Analysis for Relativistic Orbitals ............. 18

3 Structure & Bonding of $\lambda^3$-iodanes 21
  3.1 $\lambda^3$-Iodanes and the Pseudo Jahn-Teller Effect .......... 23
    3.1.1 Vibronic Coupling ................................ 23
    3.1.2 Orbital Vibronic Coupling for DFT ................ 25
    3.1.3 Pseudo Jahn-Teller Distortion of $\lambda^3$-Iodane Systems .... 25
    3.1.4 The Energy Penalty of Planarity Violation .......... 27
  3.2 Electronic Structure and The 3c-4e Bond Model ............. 28
  3.3 Relativistic Aspects of Hypervalent Bonding .............. 30
## CONTENTS

3.4 Multicenter Bonding in Diaryliodanes .................................. 34
3.5 Conclusions ................................................................. 37

4 Reactivity of Hypervalent Iodine Reagents ................................. 39
4.1 The Chemistry of Diaryliodonium Salts ................................. 41
  4.1.1 Iodine-Guided Selective Arlylation ............................... 41
  4.1.2 Bridged Diaryliodanes .............................................. 46
  4.1.3 Reductive Elimination Reaction: Mechanistic Considerations .... 52
  4.1.4 Reductive Elimination Reaction: Symmetry Considerations ...... 53
4.2 Electrophilic Trifluoromethylation ...................................... 56
  4.2.1 The Effect of Brønsted-Activation .................................. 58
  4.2.2 Transition Metal Chemistry with Hypervalent Iodine ............. 62
4.3 Conclusions ................................................................. 66
4.4 First Prospects towards a DET .......................................... 67
4.5 Supporting Information .................................................. 68

5 General Conclusions & Outlook ............................................. 71

A Appendix ........................................................................... 75
  A.1 Theoretical Notes on the DAFH Code ................................. 75
    A.1.1 Derivation of the G-Matrix for HF/KS-DFT in AO Basis ....... 75
    A.1.2 Isopycnic Transformation of the G-Matrix ....................... 77
    A.1.3 Localization Scheme ............................................... 79
    A.1.4 Localization Procedure ............................................. 80
    A.1.5 Transformation of the MO Coefficients ......................... 82

B Appendix ........................................................................... 83
  B.1 The DAFH code ............................................................ 83

C Appendix ........................................................................... 107
  C.1 Core Density Tool ....................................................... 107

Bibliography ........................................................................ 113

xii
Publications

The following publications are included in parts or in extended versions. Corresponding permissions to reproduce copyrighted material in this thesis have been obtained by the publishers as indicated.

A) H. Pinto de Magalhães, H. P. Lüthi, A. Togni, Org. Lett. 2012, 14, 3830–3833:
“Reductive Eliminations from $\lambda^3$-Iodanes: Understanding Selectivity and the Crucial Role of the Hypervalent Bond”. (Chapter 4)
Reproduced with permission from dx.doi.org/10.1021/ol3014039. Copyright 2012 American Chemical Society.

“Breaking Down the Reactivity of 3 -Iodanes: The Impact of Structure and Bonding on Competing Reaction Mechanisms”. (Chapter 3 & Chapter 4)
Reproduced with permission from dx.doi.org/10.1021/jo501714f. Copyright 2014 American Chemical Society.

C) H. Pinto de Magalhães, H. P. Lüthi, Patrick Bultinck, Phys. Chem. Chem. Phys. 2016, 18, 846–856:
“Exploring the Role of the 3-Center-4-Electron Bond in Hypervalent $\lambda^3$-Iodanes Using the Methodology of Domain Averaged Fermi Holes”. (Chapter 2, Chapter 3 & Chapter 4)
Reproduced from dx.doi.org/10.1039/c5cp05343a with permission from the PCCP Owner Societies.
Introduction

Inspiration is found everywhere if you look hard enough.

The RZA (Wu-Tang Clan)

1.1 HYPERVALENT IODINE COMPOUNDS

In the past twenty years, hypervalent iodine compounds have gained considerable attention and their potential for selective reactions is now routinely exploited in organic synthesis. Diaryliodonium salts, in particular, are versatile reagents for a number of arylation reactions. Upon addition of nucleophiles these reagents form $\lambda^3$-iodane intermediates (Figure 1.1b) that subsequently undergo a selective reductive elimination (RE). Another very illustrative example is the “Togni reagent” (Figure 1.1a) used for trifluoromethylation of a wide array of nucleophiles.[1] Among the variety of hypervalent iodine compounds, the derivatives

Figure 1.1: a) 3,3-Dimethyl-1-(trifluoromethyl)-1$\lambda^3$-2-benziodoxol (DMTB), a reagent for the electrophilic transfer of the trifluoromethyl group by reductive elimination. b) 4-Methoxyaryl-phenyl-$\lambda^3$-iodane (diaryliodane) are used for the functionalization of arenes by X. c) The model compound IH$_3$ in its T-shape equilibrium geometry and, d) the corresponding Y-shape isomerization transition state (TS). a-c) These iodanes contain a 3-center-4-electron bond, involving the iodine atom and the two bonded atoms in trans configuration.
containing formally iodine(III) and iodine(V) centers are most represented. Depending on the ligand sphere of poly-coordinated iodine centers, hypervalent iodine compounds are named as $\lambda^3$- or $\lambda^5$-iodanes, respectively, according to IUPAC recommendations.[2] The unusual reactivity of iodanes is strongly tied to the bonding properties of the iodine center. Even though iodine, a 5p-element, already belongs to the late p-block of the main group elements, it is predominantly affected by scalar relativistic effects.* With its moderate electro-negativity in addition, iodine is predestined to form hypervalent bonds.[3]

**The Concept of Hypervalence**

Hypervalent bonding as found in $\lambda^3$-iodanes is observed in molecules containing main group elements (groups 13-18), which violate the Lewis octet rule by accommodating more than eight electrons in their valence shell.[4] This phenomenon is not based on relativistic effects, but on the atomic shell structure.[3,5] In principle, the p-shells are larger and more diffuse than the s ones, with the exception of the second shell. The similarity of the radial extent of 2s- and 2p-shell is, in fact, a decisive factor that determines the special role of the 2p-elements, which is considered the first row anomaly.[5,6] In the later p-block, on the other hand, the s- and p-shells are increasingly disparate due to the contraction of the valence s-shell. The result is the occurrence of “hybridization defects” with serious consequences for hypervalent bonding.[3,5]

According to Musher,[7] hypervalent molecules can be divided in two classes: The first type (HV$_I$) shows only minimal hybridization and forms multi-center bonds (e.g. SCl$_4$, IF$_3$). The HV$_{II}$ class molecules, on the other hand, are arranged highly symmetricly involving the s-valence shell in the hypervalent bonds (e.g. XeO$_4$, PF$_5$, IF$_7$). $\lambda^3$-Iodanes are classified as HV$_I$ and the interaction between the iodine and its substituents in a $\lambda^3$-iodane has been described in terms of 3-center-4-electron (3c-4e) bond model as presented by Hach, Rundle and Pimentel.[8–11]

*Spin-orbit coupling splits the degenerate p-orbitals into one $p_{1/2}$ and two $p_{3/2}$ components. In iodine this effect is small and can be neglected in qualitative considerations.
1.1 HYPERVALENT IODINE COMPOUNDS

The 3-center-4-electron Bond

According to the 3c-4e bond model, the interaction between iodine and its equatorial ligands is described by three molecular orbitals (MOs) exhibiting bonding, non-bonding, and anti-bonding character in this order on the energy scale (see Figure 1.2a). The two lower-energy MOs are occupied by two electrons each, and the node at the iodine center in the non-bonding MO is responsible for the strongly polarized hypervalent bonds (Figure 1.2). In consequence, the most electron withdrawing substituents are found in trans position.[12] This molecular orbital based model allows to understand many structural and electronic features of these compounds in view of a pseudo Jahn-Teller (PJT) effect: the T-shape \( \lambda^3 \)-iodanes isomerize via a Y-shape geometry and maintain planarity of the hypervalent region in all chemical reactions. The impact of the PJT effect is illustrated later for the model compound IH\(_3\). That is, an in-plane distortion of the high symmetry Y-shape (D\(_{3h}\)) geometry towards a T-shape (C\(_{2v}\)) structure, leading to the stabilization of the 3cb\(_{nb}\) orbital (Figure 1.2a) through interaction with a virtual orbital of the same symmetry (see Section 3.1.3). On the other hand, the out-of-plane distortion of the D\(_{3h}\) structure towards a pyramidal (C\(_{3v}\)) configuration comes with an energy penalty due to unfavorable mixing of the non-bonding 3cb\(_{nb}\) orbital with a lone pair of the iodine center.

Figure 1.2: A schematic representation of the 3-center-4-electron bond in \( \lambda^3 \)-iodanes (a) along with the corresponding natural localized molecular orbitals (NLMOs) of bromo 1,1’-biphenyl iodane (b). The orbitals are labeled as 3-center bonds (3cb) of bonding, non-bonding (nb) or anti-bonding (*) character.
Multicenter Bonding in p-Block Elements

Later p-block elements show hybridization defects and, at the same time, incorporate as little s-character in their bonding orbitals as possible. Thus, in these elements pure p-bonding is generally favored and the resulting hypervalent bonds are stabilized by multi-center bonding of the ligands with a shared p-orbital of the central atom (see Figure 1.3).\[5\] However, the occurrence of multi-center bonding in hypervalent compounds is still the subject of an ongoing debate, and the different approaches often lead to contradictory views.\[3,5,11,13,14\]

Most recently, Dunning and co-workers, with the Recoupled Pair Bond model, an approach based on General Valence Bond (GVB) theory, presented arguments against multi-center bonding.\[6\] Their “recoupled pair bond dyad” corresponds to two very polar but equivalently localized 2-center bonds, which is in contrast to the delocalized 3c-4e bond. Kaupp, on the other hand, interprets the partially ionic resonance structures in Valence Bond (VB) language as equivalent to multicenter bonding and negative hyperconjugation in MO language.\[5\]

![Figure 1.3: Illustration of multi-center bonding by the methodology of Domain Averaged Fermi Holes analysis. Displayed is the 3cb domain natural orbital of triphenyl-λ^3^-iodane.](image-url)
1.2 THE CHEMISTRY OF $\lambda^3$-IODANES

Hypervalent iodine compounds are very useful for many organic transformations, both as reagents for a variety of functionalizations and as catalysts for oxidative reactions.$^{[2,15,16]}$ The unusual reactivity of these reagents allows for fast reactions, even with a closed shell electronic structure. This leads to broad range of reactivity patterns involving isomerization of T-shape configurations, reductive elimination of the substituents, or even radical reactions (see Section 4.1.2).

Under standard conditions, $\lambda^3$-iodanes are only stable if bearing at least one aromatic group.$^{[15]}$ Therefore, synthetic applications are focused on the use of diaryliodanes (see Section 4.1.1), which are encountered as reagents as well as reactive intermediates. The latter ones are observed in the diaryliodonium salt chemistry,$^{[17]}$ in which rapidly equilibrating isomeric $\lambda^3$-iodane intermediates are formed by the capture of nucleophiles as an additional ligand. In the application of these iodonium salts containing two different aryl groups selectivity issues arise as to which group will be transferred to a nucleophile (Figure 1.4).

![Figure 1.4: Conversion of a diaryliodonium salt with an azide resulting in the selective functionalization of the phenyl group via rapid isomerization of the iodane intermediates. All reaction products are the result of a reductive elimination.](image)

The impressive mechanistic diversity of $\lambda^3$-iodane reagents also opened new routes for the electrophilic trifluoromethylation by Togni reagents. By introducing structural constraints, the reactivity of e.g. DMTB can be designed
to be reminiscent of organometallics (see Section 4.2). In order to access the most reactive form of DMTB, an activation process involving Brønsted acids or transition metals is usually performed\cite{18,19}, having a substantial impact on the nature of the 3c-4e bond. Hence, this activation process will have an effect on the basic course of the reaction, that is an iodine-guided reductive elimination.

### 1.3 OUTLINE OF THE THESIS

The research presented in this thesis targets the understanding of the structure and reactivity of hypervalent compounds, in particular $\lambda^3$-iodanes. Over the past few years, the development of synthetic methods incorporating hypervalent iodine has been booming, and much is known experimentally about the properties and the reactivity of iodanes. This opened a great opportunity for theory to contribute to this area of chemistry, and to assist to its further development. There are three main topics that will be addressed:

I. Mechanistic studies: As part of this research, the most important types of reactions involved in the functionalization of organic nucleophiles will be visited using static quantum chemical methods (Chapter 3 & Chapter 4). This setting allows to contribute to the understanding of the reactions observed experimentally and to find appropriate measures to improve selectivity or open alternative routes.

II. Chemical bonding: The properties and features of the chemistry of hypervalent iodine compounds are explored to cast complex quantum chemical investigations into simple chemical models. In terms of chemical bonding, the main tool is Density Functional Theory (DFT) along with Natural Bond Orbital (NBO) analysis, as well as Domain Averaged Fermi Holes (DAFH) analysis. Their application on model systems is particularly promising to form a new basis for a more general understanding of hypervalent bonding (Chapter 2 & Chapter 3).
III. Quantum chemistry related issues: The importance of relativistic effects, in particular spin orbit coupling, will be addressed in this context. In order to accommodate the requirement for a sophisticated assessment of spin orbit effects, relativistic exact-two- and four-component computations will be performed (Chapter 3).

These studies are part of a joint experimental and computational research project with the laboratory of Togni, in which hypervalent iodine based trifluoromethylation agents are being developed.\cite{1,20} Accordingly, the goal of this thesis is also to open up new perspectives on structure and bonding of $\lambda^3$-iodanes. The provided insight into the reactivity of hypervalent iodine reagents hopefully allows to establish guidelines for new experiments, and enables, in the best case, optimization of the performance of existing reagents or to tailor novel iodane reagents for the functionalization of specific targets.
Methodology and Theoretical Background

People know what they do; frequently they know why they do what they do; but what they don’t know is what they do does.

Michel Foucault

Computational chemistry has nowadays reached a stage, in which it is elevated to a routine part of chemical research. The continuing progress in the development of new computational tools of quantum chemistry, in addition, opened the possibility to perform reliable theoretical calculations on real, chemically interesting systems. However, the complexity of the wave functions remains a major challenge for their interpretation and it is ambitious to find direct links between the results of calculations and classical chemical concepts of bonds. In this light, the design of auxiliary methods is of particular importance to establish a basis for the interpretation of wave functions and for extracting from them the desired structural information.

This chapter elaborates some approaches that are particularly useful in the context of this work. Section 2.2 illustrates the systematic analysis of the exchange-correlation pair hole matrix, a two-electron measure, suitable for visualization, even in systems with complicated bonding patterns. To provide insight into the relativistic electronic structure, Projection analysis of relativistic orbitals is briefly sketched in Section 2.3. At the end of this chapter, we shall be equipped with a set of tools and recipes that will be applied to the chemical problems discussed in the following chapters.
2.1 PARTITIONING OF THE ELECTRON DENSITY IN THE LIMIT OF THE SCF APPROXIMATION

The self-consistent field (SCF) approach is based on a single-particle picture of electronic systems, each electron occupying a one-particle state (orbital). Canonical molecular orbitals (CMOs) obtained from such SCF calculations, within the framework of Hartree-Fock (HF) or Kohn-Sham density functional theory (KS-DFT), are the result of minimizing the total energy by including the Coulombic interaction of single electrons with the other electrons and the nuclei in average. In order to diagonalize the Fock operator, the CMOs must span irreducible representations of the molecular point group and are, in consequence, generally delocalized over the whole molecular framework. This yields well-defined orbital energies, which are suitable for the interpretation of experimental molecular spectra. The simplicity of the single-particle picture allows for a general understanding of chemistry, its delocalized nature, however, does typically not correspond to the classical Lewis-Linnett picture of localized bonds and lone pairs.\[4\] For the use of chemical concepts, it is usually necessary to transform the CMOs into localized orbitals, which are much more chemically intuitive.\[21–24\] There are various approaches available to extract information about bonding of canonical SCF molecular orbitals. The focus of this chapter, however, lies on techniques for the partitioning of the electron density.

2.1.1 Natural Orbital Decomposition

Many difficulties in quantum chemistry are related to complicated the form of the wavefunction and to the extraction of any physically relevant information from its.\[25\] The solution of the Schrödinger Equation requires integrals over 4N coordinates, all observables of interest, however, can be expressed as expectation values of operators involving at most two electronic sets of coordinates (as pair-wise interactions do dominate). In order to account for this two-electron interactions it is useful to change the focus from the traditional Fock space to real space, resulting in orbital invariant quantities. Hence, consider the general
2.1 PARTITIONING OF THE ELECTRON DENSITY

form of the product of a wavefunction

$$\gamma(x_1, x_2, \ldots, x_N; x'_1, \ldots, x'_N) := \Psi(x_1, x_2, \ldots, x_N)\Psi^*(x'_1, x'_2, \ldots, x'_N),$$

(2.1)

that is, the Nth order density matrix for a pure state. In Eq. (2.1) $x_i$ stands for the collection of both spatial and spin coordinates of electron $i$ ($x_i = r_i, \sigma_i$). This expression resembles the probability distribution of the system according to the Born interpretation of the wavefunction $\rho(x_1, x_2, \ldots, x_N)$, which corresponds to its diagonal elements (all primed coordinates are equal to their unprimed counterparts)

$$\gamma(x_1, x_2, \ldots, x_N; x'_1, \ldots, x'_N) = \rho(x_1, x_2, \ldots, x_N).$$

(2.2)

Note that $\gamma(x_1, \ldots, x_N; x'_1, \ldots, x'_N)$ and $\rho(x_1, \ldots, x_N; x'_1, \ldots, x'_N)$ are used interchangeably, depending on the particular context. Within the limit of the SCF approximation, knowledge of the first-order reduced density matrix $\gamma(x_1, x'_1)$ is sufficient to calculate the total electronic energy\[^{25}\]

$$\gamma_{HF}(x_1, x'_1) = N \int \Psi_{HF}(x_1, \ldots, x_N)\Psi_{HF}^*(x'_1, \ldots, x_N) d x_2 \ldots d x_N.$$  

(2.3)

Moreover, $\gamma(x_1, x'_1)$ uniquely determines expectation values of all one-electron operators\[^{22}\]. Eq. (2.3) reveals that by the integration of the electron density, any single-particle property can be extracted from the wavefunction. This corresponds to a partitioning of a many-particle system into a one-electron subsystem. Since $\gamma(x_1, x'_1)$ is a function of two variables, it can be expanded in the orthonormal basis of the HF orbitals $\{\phi_i\}$

$$\gamma_{HF}(x_1, x'_1) = \sum_{i}^{\text{orb}} \eta_i \phi_i(x_1)\phi_i(x'_1) = 2 \sum_{i}^{\text{occ}} \phi_i(x_1)\phi_i(x'_1).$$

(2.4)

The diagonal elements of $\gamma_{HF}$ can be regarded as occupation numbers $\eta_i$, and take a particularly simple form of $\eta_i = 2$ if occupied, and $\eta_i = 0$ else. For the case of a general wavefunction, $\gamma$ is not diagonal in the basis of HF orbitals\[^{26}\]. However, a new orthonormal basis $\{\psi_k\}$ is obtained by the means of unitary
transformation $\psi_k = \sum_i U_{ki} \phi_i(x_1)$:

$$\gamma(x_1, x'_1) = \sum_{l} \lambda_{li} \psi_l(x_1) \psi_l(x'_1), \quad (2.5)$$

resulting in maximal occupied orbitals within the Pauli restriction. The basis $\{\psi_k\}$ is denoted as natural orbitals, and the diagonalization of $\gamma(x_1, x_1)$ considered the natural orbital decomposition of the electron density. In terms of Natural Bond Orbital (NBO) analysis \cite{27}, this procedure is restricted to atomic blocks. The resulting orthonormal set corresponds to maximal occupied (i.e. the best shaped) atomic orbitals (AOs) in the local ligand sphere of the molecular framework. Such a natural atomic orbitals (NAO) basis consists of set of hydrogen-like atomic orbitals ($1s, 2s, \ldots, 2p, 3p$, etc.). By defining the connectivity inside a molecule in a next step, adjacent atoms are connected to form bonding, anti-bonding and non-bonding (core and lone pair) orbitals.

The analysis of Domain Averaged Fermi Holes (DAFH), introduced in the next section, is closely related to the natural orbital decomposition, relying, however, on the basis of a different density (exchange-correlation hole matrix). This alternative approach benefits from dropping the restriction of the connectivity of the atoms, providing a bonding pattern genuine to the nuclear configuration of the molecule.

## 2.2 DOMAIN AVERAGED FERMI HOLES

The electronic wave function, obtained as a (approximate) eigenfunction of the Hamiltonian operator, contains all possible information on the electronic structure of a molecule, including the correlated behavior of electrons. As is well-known, by going from classical to quantum mechanics and given a proper (approximate) wave function, the joint probability of finding two electrons at some coordinates $x_1$ and $x_2$ differs from the product of the individual probabilities for each electron separately. It is in this departure from classical behavior that the chemical bond finds its roots. The exchange-correlation hole matrix $h^{xc}(x_1, x_2; x'_1, x'_2)$ is a two-electron measure that reflects this non-classical beh-
2.2 DOMAIN AVERAGED FERMI HOLES

behavior, defined here as:

\[ h^{xc}(x_1, x_2; x'_1, x'_2) = \rho(x_1, x'_1)\rho(x_2, x'_2) - 2\rho^{(2)}(x_1, x_2; x'_1, x'_2) \]  \(\text{(2.6)}\)

Note that \( h^{xc}(x_1, x_2; x'_1, x'_2) \) is an extension\[^{[28]}\] of the more often encountered exchange-correlation hole to a matrix formulation to allow obtaining properly defined eigenvalues and eigenvectors. Also note that often slightly different expressions may be found depending on the normalisation considered in the definition of the second order density matrix \( \rho^{(2)}(x_1, x_2; x'_1, x'_2) \) (here \( N(N-1)/2 \) with \( N \) the number of electrons) and depending on the sign chosen in \( h^{xc} \).

There are two sources of electron correlation: collective spin and permutation symmetry requirements due to their fermionic character (Fermi correlation), and Coulomb correlation from the repulsion between the electrons.\[^{[29]}\] As a matter of fact, \( h^{xc} \) clearly integrates to \( N \) and captures the essence of chemical bonding even already at the level of single determinant theory. Notably, an electron with given spin \( \sigma_i \) digs a hole around itself where the probability of finding another electron with the same spin is strongly reduced.\[^{[29-31]}\] In order to illustrate this behavior, we consider the conditional probability \( \rho^{\text{cond.}}(x_1|x_2) \) of electron 1 in relation to a second electron and its departure from the single-particle density

\[ \rho(x_1) - \rho^{\text{cond.}}(x_1|x_2) = h(x_1|x_2), \]  \(\text{(2.7)}\)

which is the definition of the so-called Fermi hole.\[^{[32]}\] The spin-integration of one particle of \( h(x_1|x_2) \) leads to the following cases:

\[ \int h(x_1|x_2) \, d\sigma_1 = \begin{cases} 1 & \text{if } \sigma_1 = \sigma_2 \\ 0 & \text{if } \sigma_1 \neq \sigma_2 \end{cases} \]  \(\text{(2.8)}\)

That implies the exclusion of a same spin electron from the pool of particles, but not for the electron with a different spin. Based on this observation, Ponec et al.\[^{[33,34]}\] derived the so-called Domain Averaged Fermi Hole (DAFH) analysis where first one limits \( h^{xc}(x_1, x_2; x'_1, x'_2) \) to the case where all electronic coordinates have the same spin. This results in a spinless \( g^{xc}(r_1, r_2; r'_1, r'_2) \):

\[ g^{xc}(r_1, r_2; r'_1, r'_2) = \sum_{\sigma_1, \sigma_2} \int d\omega_1 \, d\omega_2 \, \delta_{\sigma_1 \sigma_2} \, h^{xc}(r_1 \sigma_1, r_2 \sigma_2; r'_1 \sigma_1, r'_2 \sigma_2) \]  \(\text{(2.9)}\)
This way, one can examine, given a specific spin and position of one of the electrons (say \( r_1 = r'_1 \)), the exchange correlation hole as a function of the position of the other electron (say \( r_2 = r'_2 \)). For the illustration of the spinless case, integration of \( h(r_1 | r_2) \) is performed over one space coordinate. This leads again to the exclusion one particle, which determines the effective single-electron shape of one of the systems particles.

The second, key idea in the methodology of DAFH is to condense the functions derived from the holes \( g^{xc}(r_1, r_2; r'_1, r'_2) \) to some domain in the molecule and decomposed it into one-particle subsystems. The resulting \( g^{xc}_{\Omega}(r_2; r'_2) \) are obtained through integration of \( g^{xc}(r_1, r_2; r'_1, r'_2) \) over, say, electron 2 in a specific domain of the molecule, often a single atom (\( \Omega = \Lambda \)) in the molecule (AIM):

\[
g^{xc}_{\Omega}(r_2; r'_2) = \int g^{xc}(r_1, r_2; r'_1, r'_2) w_{\Omega}(r_1) \delta(r_2 - r'_2) \, dr_2 \, dr'_2 \tag{2.10}
\]

In Eq. (2.10) the integration is assumed to be expressible in terms of a 3D-domain in position space using a domain weight function \( w_{\Omega} \) although equivalent expressions can be derived in Hilbert space to yield a Mulliken\cite{35} type DAFH\cite{33,34}. Moreover, also in 3D position space defined AIM, different results may be found\cite{28} depending on whether one uses e.g., QTAIM\cite{36-38} or Hirshfeld-I\cite{39-42}. The latter differences are, however, fairly limited and in the remainder we use QTAIM throughout. Eq. (2.10) becomes particularly simple at the single Slater determinant level of theory, as in Hartree-Fock theory, thanks to the Löwdin relationship between density matrices of increasing order.\cite{43} Hence, within the LCAO-MO framework \( h^{xc} \) will reduce to

\[
h^{xc}(r_1, r_2; r'_1, r'_2) = \sum_{ij}^{or\beta} \phi_i(r_1) \phi_i^+(r'_2) \phi_j(r_2) \phi_j^+(r'_1) \tag{2.11}
\]

\[
= \sum_{ij}^{oc\beta} \eta_i \phi_i(r_1) \phi_i^+(r'_2) \eta_j \phi_j(r_2) \phi_j^+(r'_1) .
\]

Here \( \{\phi_i\} \) are the molecular orbitals with occupation numbers \( \eta_i \) and the latter simplification is given, because we only consider closed shell singlet molecules in the present work (both spin density matrices are equal). The same equations result from a Kohn-Sham Density Functional Theory approach although one
should take into account that there the Slater determinant cannot be considered to stand on the same footing as in Hartree-Fock theory. Nevertheless, experience has shown that very useful insights may be obtained from Kohn-Sham based delocalisation indices which are based on DAFH. By using Eq. (2.12) results in the following derivation

\[
g^{xc}_{\Omega}(\mathbf{r}_1, \mathbf{r}_1') = \sum_{ij}^{occ} \phi_i(\mathbf{r}_1) \int \mathbf{w}_\Omega(\mathbf{r}_2) \phi_j(\mathbf{r}_2) \phi_j^*(\mathbf{r}_2') \delta(\mathbf{r}_2 - \mathbf{r}_2') \, d\mathbf{r}_2 \, d\mathbf{r}_2' \, \phi_i^*(\mathbf{r}_1') 
\]

\[
= \sum_{ij}^{occ} \phi_i(\mathbf{r}_1) S^\Omega_{ij} \phi_j^*(\mathbf{r}_1') = \sum_{ij}^{occ} \phi_i(\mathbf{r}_1) G^\Omega_{ij} \phi_j^*(\mathbf{r}_1') \quad (2.12)
\]

for the \(g^{xc}_{\Omega}\) with its discrete representation \(G^\Omega_{ij}\). Here the integration was performed over a domain \(\Omega\) that may be a single atom or a union of atoms. \(S^\Omega_{ij}\) is an element of the so-called Domain Overlap Matrix. If the domain contains only a single atom, i.e. \(\Omega = A\), it is known as Atomic Overlap Matrix (AOM):

\[
S_{ij}^A = \int \phi_i^*(\mathbf{r}_1) w_A(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \, d\mathbf{r}_1 , \quad (2.13)
\]

and according to Eq. (2.12) \(S_{ij}^A = G_{ij}^A\). For visual interpretation the matrix \(g^{xc}_{A}(\mathbf{r}_1; \mathbf{r}_1')\) can then be expressed in diagonal form

\[
g^{xc}_{A}(\mathbf{r}_1, \mathbf{r}_1') = \sum_k^{occ} \varphi_k(\mathbf{r}_1) \tilde{G}^A_{kk} \varphi_k^*(\mathbf{r}_1') = \sum_k^{occ} \eta^A_k \varphi_k(\mathbf{r}_1) \varphi_k^*(\mathbf{r}_1') , \quad (2.14)
\]

with \(G^A_{kk} = \eta^A_k\) a new set of one-particle functions \(\varphi_k = \sum_i X_{ki}^A \phi_i\) related by unitary transformation. Costales et al. emphasized the analogy to the natural orbital decomposition of a density matrix by naming the new basis of single-particle functions \(\varphi\) “domain natural orbitals (DNOs)” and the corresponding eigenvalues as “occupation numbers”. As a matter of fact, the choice of atomic basins as domains results in chemically intuitive DNOs like “core orbitals” \((\eta^A_i = 2)\), “lone pairs” \((\eta^A_i \approx 2)\) and “broken valences” (or “bond orbitals”, \(\eta^A_i < 2\)) with the corresponding populations (e.g. Figure 2.1). Note, however, that again like in density matrices, one can independently diagonalise the \(\alpha\) and \(\beta\) spin matrices of Eq. (2.9). Given that we here consider only closed shell singlet molecules in the present work, both matrices are equal.
2 METHODOLOGY AND THEORETICAL BACKGROUND

Figure 2.1: Illustration of two selected domain natural orbitals (DNOs) showing the iodine basin inside of IH$_3$: a) a core d-orbitals, b) a 2-center bonding (2cb) orbital, which reaches into the neighboring hydrogen domain, and c) the corresponding 2cb DNO of the hydrogen domain. Whereas the occupation number of the core orbital is close to 2.0, the 2cb orbital will show a “broken valence”, i.e. an occupation number typically near 1.0.

2.2.1 Practical Notes on DAFH

DAFH analysis proceeds by choosing the specific domains $\Omega$ and computing the occupation numbers and DNO’s. The latter can be visualised and core orbitals and lone electron pairs are easily identified through their occupation numbers and shapes. For the broken valences, visualisation already suggests what chemical bond they participate in and by computing the DNO’s of the suspected bonded fragment, one can confirm the bonding pattern. This is then further supported by summing the occupation numbers for both DNO’s, resulting in a value close to two. Of key importance in the present work is that in case of multicenter bonding, the simple addition of two QTAIM domains does not lead to the expected sum of two. Instead, more domains are needed. DNO’s are moreover not necessarily directed following the bonds as a Lewis picture would urge to. In order to obtain such DNO’s, an isopycnic transformation\cite{22,46} is performed. This will orient the DNOs to achieve the best possible electron pairing in the specific molecular framework, that, in many cases, corresponds to the Lewis picture. The transformation procedure is based on maximising the localisation sum

$$\sum_k \eta_k^2 \sum \sum A |S_{kk}^A|^2 = \sum_k \eta_k^2 L_k .$$

(2.15)
2.2 DOMAIN AVERAGED FERMI HOLES

The localisation index $L$ consists of a summation over all orbitals of the sum of squared diagonal domain overlap matrix elements over all atoms $A$. The key behind this transformation is that the matrix $\mathbf{g}_{\Omega}(r_2; r'_2)$ remains unchanged and retains the same form of expression. As the eigenvalues $\eta^A_i$ are obviously non-degenerate in most cases, such a transformation is non-unitary and therefore the same expression involving only diagonal elements is only possible abandoning the orthonormality of the localised DNO’s. The localization index $L_k = \sum_A |S^A_{kk}|^2$ is a measure of deviation from atom-centered orbitals. Thus, the maximization of the localization sum $L$ defines orbital transformations $\tilde{\phi}_i = \sum_k X_{ik}^* \varphi_k$, that increase the overlap in bonding regions, and decrease it everywhere else, within the boundaries of paired electrons. Only valence DNOs are (significantly) affected by the transformation, as the core and some lone pair DNOs are already (nearly) fully occupied. If the canonical bond DNOs already show a strong orientation for inter-domain electron coupling, localized orbitals differ marginally. Hence, the analysis of the evolution of DNOs by isopycnic transformation allows to draw conclusions about the nature of multicenter bonding.

2.2.2 Workflow of the DAFH Analysis

The program for the posteriori analysis by the methodology of DAFH was developed in house and is printed in full length in Section A.1.1. In order to perform a DAFH analysis it is necessary to operate with different programs, as sketched in the work-flow in Figure 2.2: QTAIM partitioning of the electron density into atomic basins has to be performed with the AIMALL program suite on top of DFT wavefunctions obtained by geometry optimization with Gaussian 09. QTAIM integrations in the presence of pseudopotentials were made possible by proper addition of core densities in the set of natural orbitals leading to the total density (see "core density tool" in Section C.1).

\footnote{In the present context, the term canonical refers to the standard (orthonormal) DNOs obtained by diagonalization of domain averaged Fermi hole (2.12).}
2 METHODOLOGY AND THEORETICAL BACKGROUND

**Electronic structure calculation**

- **Density matrix of CMOs**
  \[ \rho(r) = 2 \sum_i c_{ij} |\Phi_i(r)| \langle \Phi_j(r) | \]

- **Formulation in LCAO-MO**
  \[ \sigma^{xc}(r_1, r_2; r'_1, r'_2) = 2 \sum_{ij} |\Phi_i(r_1)| \langle \Phi_i(r_2) | \times |\Phi_j(r_2) \rangle \langle \Phi_j(r_1) | \]

**Decomposing pair density & divide space into atomic subspaces**

- **1-particle xc-density (Fermi hole)**
  \[ g_A(z_1, z'_1) = \sum_{ij} S_{ij}^0 |\Phi_i(z_1)| \langle \Phi_i(z'_1) | \]

**Diagonalize atomic subblocks**

- **Maximizing localization sum**
  \[ L = \sum_A (k|k)^A \rightarrow L = \sum_k \sum \eta_k \eta_k \]

- **Isopycnic transformation: maximal electron pairing**
  \[ \tilde{\Phi}_i = \sum_k c_{ik} |\phi_k | \]

- **Transform orbital coefficients**
  \[ g_A(z_1) = \sum_l \eta_l |\tilde{\Phi}_l(z_1) \rangle \langle \tilde{\Phi}_l(z_1) | \]

---

**Figure 2.2**: Overview of the DAFH procedure: work-flow of DAFH (center), supplemented by the interfaces to the computational tools (left) and the theoretical formulations (right).

### 2.3 PROJECTION ANALYSIS FOR RELATIVISTIC ORBITALS

When considering relativistic effects, two main features determine chemical bonding, namely the orbital energies and the spatial extent of the orbitals of the atoms involved. In heavy elements, these atomic properties are considerably departing from the non-relativistic picture.\(^3\) While scalar-relativistic effects are addressed in all of our calculations by the incorporation of a relativistic effective core potential for iodine, the influence of spin-orbit (SO) coupling on chemical bonding is not considered. Spin-free relativistic effects change only the magnitude of bonding because the orbital symmetries stay the same. The coupling of spin and orbital angular momentum, on the other hand, has implications for the one-particle functions: e.g. the splitting of \( p_{1/2} \) and \( p_{3/2} \) is in particular relevant for the bonding of molecules with heavy p-block elements.\(^47\)
2.3 PROJECTION ANALYSIS FOR RELATIVISTIC ORBITALS

In a two- or four-component relativistic model, spinors are the solutions of the Dirac wave equation for single electrons. Therefore, linear combinations of atomic spinors (LCAS) already include SO interactions and allow an interpretation of their impact in structure and bonding. In close relation to the Mulliken population analysis, atomic contributions are projected from the relativistic orbitals that have been generated in a self-consistent manner in the full molecular basis. But instead of scalar basis functions, the molecular orbitals are given as two- or four-component functions. In such a projection analysis,[48] the MOs \( |\Psi_{k}^{\text{MO}}\rangle \) are first expanded by the occupied orbitals of the constituent atoms \( |\psi_{i}^{A}\rangle \)

\[
|\Psi_{k}^{\text{MO}}\rangle = \sum_{i,A} |\psi_{i}^{A}\rangle c_{ik}^{A} + |\psi_{k}^{\text{pol}}\rangle,
\]

including the specific expansion coefficients \( c_{ik}^{A} \). If a significant electron density cannot been assigned, orthogonal polarization orbitals \( |\psi_{k}^{\text{pol}}\rangle \) have to be introduced. Together with these polarization orbitals, the occupied atomic orbitals form the reference orbital space. Finally, the coefficients \( c_{qi}^{B} \) of the expansion into the reference orbitals are determined by projection:

\[
\langle \psi_{i}^{A} | |\Psi_{k}^{MO}\rangle = \sum_{B} \sum_{q \in B} \langle \psi_{i}^{A} | \psi_{q}^{B} \rangle c_{qi}^{B},
\]

In combination with molecular operators, a projection analysis onto an atomic basis helps to reveal essential atomic contributions for a specific property. For the investigation of relativistic effects, it is of particular interest to study the atomic contributions to the contact density, which is directly related to the experimental isomer shift in Mössbauer spectroscopy, where the contact density has proven to give valuable information about bonding properties and the geometrical arrangement.[49–53]
Structure & Bonding of $\lambda^3$-iodanes

The exploration of the nature of bonding in hypervalent molecules and, in particular, of multicenter bonding is still the subject of a dynamical field of research.\cite{3,5,11,13,14} Therefore, the primary aim of this chapter is to provide a qualitative understanding of multicenter bonding for the specific case of $\lambda^3$-iodanes and to reach for versatile conceptual tools. Equipped with the partitioning schemes introduced in Chapter 2, it is now possible to assign quantum chemical properties to concepts of structure and bonding. In order to break down the physically meaningful basis of these orbital-based theories, the electronic structure of iodane model systems were explored in great detail (Section 3.1 & Section 3.1.3). The investigations of the model systems are then completed by the study of a series of real chemical systems, which provided a well-defined ordering scheme for the reactivity of $\lambda^3$-iodanes.
Computational Details

All *ab initio* computations presented in this work are based on ground state geometries optimized for closed shell singlet states by means of density functional theory (DFT), using the quantum chemical package Gaussian 09 (G09 Rev D.01). The B3LYP exchange-correlation functional\(^{[55–58]}\) was employed along with the Cartesian aug-cc-pVTZ-PP basis sets for the model systems (*Section 3.1*), and cc-pVTZ-PP for the diaryliodane series (*Section 3.2*).\(^{[59]}\) Scalar relativistic and scalar spin-orbit effects were considered for the iodine atom by the use of a semi-local electron core potential, the Stuttgart-Koeln-MCDHF-RSC-28-ECP.\(^{[60]}\) All energies are given as approximate Gibbs free energies obtained from vibrational analysis at a temperature of 298.15K and standard conditions (unless otherwise noted).

*For Section 3.1:*
Natural localized molecular orbitals (NLMOs) were obtained from the natural bond orbitals (NBOs) using the NBO program version 3.1.\(^{[61]}\)

*For Section 3.2 & Section 3.4:*
QTAIM partitioning of the electron density into atomic basins was performed with the AIMALL (Version 14.04.17) program suite.\(^{[62]}\) The QTAIM integrations in the presence of pseudopotentials were made possible by proper addition of core densities in the set of natural orbitals leading to the total density. The program for a posteriori analysis by the DAFH methodology was developed in house and is printed in full length in *Chapter A*.

*For Section 3.3:*
All molecular calculations of this section have been carried out with the DIRAC14 program package\(^{[63]}\) on top of the non-relativistic DFT geometries, which were obtained with the specifications given above. Exact-two-component DFT based on a Dirac-Coulomb (DC) Hamiltonian was employed together with the use of the B3LYP exchange-correlation functional and along with atom-centered all-electron Dyall basis sets of triple-ζ quality.\(^{[64–69]}\)
### 3.1 $\lambda^3$-IODANES AND THE PSEUDO JAHN-TELLER EFFECT

At a first glance, one might expect the model $\lambda^3$-iodane compound IH$_3$ to have a trigonal planar $D_{3h}$ (Y-shape) rather than a $C_{2v}$ (T-shape) structure (see Figure 3.1). However, one consequence of high symmetry are degenerate electronic states that may couple to nuclear motion leading to lower symmetry configurations (vibronic coupling). In fact, such a high symmetry configuration is located on an intersection of the potential energy surface (PES), where the strong vibronic coupling results in a rearrangement of the molecule (Jahn-Teller effect).

**Figure 3.1:** Valence electron configuration of trigonal planar IH$_3$. The MO energy levels are labeled according to the molecular $D_{3h}$ symmetry.

#### 3.1.1 Vibronic Coupling

In the Born-Oppenheimer approximation, the dynamics of nuclear motion is not considered and, thus, vibronic coupling is considered a non-adiabatic effect. From a Jahn-Teller (JT) perspective, these effects are perturbations to the high symmetry reference configuration, resulting in deformation of the PES. Moreover, the involved (pseudo-)degenerate electronic ground states can mix sufficiently strong, when nuclear displacements occur. Having low lying excited states (pseudo degeneracy), vibronic coupling can lead to an instability of the ground state resulting again in a molecular rearrangement (pseudo Jahn-Teller (PJT) effect).
3 STRUCTURE & BONDING OF \( \lambda^3 \)-IODANES

For small displacements \( Q \) of the nuclei the potential energy term \( V(\mathbf{r}, Q) \) of the Schrödinger equation can be expanded in a Taylor series

\[
V(\mathbf{r}, Q) = V_0(\mathbf{r}, 0) + \sum_{\alpha} \left( \frac{\partial V}{\partial Q_\alpha} \right)_0 Q_\alpha + \sum_{\alpha, \beta} \left( \frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta} \right)_0 Q_\alpha Q_\beta + \mathcal{O}(Q),
\]

(3.1)

neglecting the terms higher than second order \( \mathcal{O}(Q) \) in the harmonic approximation. The first term \( V_0(\mathbf{r}, 0) \) of Eq. (3.1) represents the “static” potential energy with fixed nuclei, depending only on the electron coordinates \( \mathbf{r} \). The dynamical term includes all distortions along the normal modes \( Q \xi \) and, therefore, accounts for vibronic coupling.

When considering the electron configuration of \( \lambda^3 \)-iodanes (Figure 3.1), only the PJT effect contributes to the coupling terms with one single normal mode \( Q \). The harmonic nuclear interaction of the electronic ground state \( \Psi_0 \) in Eq. (3.1) results in a primary force constant \( K_0 \), determining the basic shape of the PES. The consequence of any perturbation of a two-level system (coupling a ground state \( \Psi_0 \) to an excited state \( \Psi_n \)) on the PES is given by the general force constant

\[
K = K_0 + K_v = \left\langle \Psi_0 \left| \frac{\partial^2 V}{\partial \mathbf{Q}^2} \right| \Psi_0 \right\rangle - 2 \sum_n \frac{\left\langle \Psi_0 \left| \frac{\partial V}{\partial \mathbf{Q}} \right| \Psi_n \right\rangle^2}{E_0 - E_n},
\]

(3.2)

containing the vibronic contribution \( K_v \) and the electronic energy levels \( E_n \).

Closer inspection of Eq. (3.2) reveals that the vibronic contribution is accounting for partial relaxation of the electron cloud upon nuclear displacements, and implies an instability of the system if \( |K_v| > |K_0| \). Based on the from of the integral in \( |K_v| \), the symmetry of the distortion \( Q \) is determined by the selection rule for the elements of the linear vibronic coupling matrix\(^*\)

\[
H_Q = \left\langle \Psi_0 \left| \frac{\partial V}{\partial \mathbf{Q}} \right| \Psi_n \right\rangle.
\]

After all, JT and PJT vibronic effects are not restricted to a narrow group of symmetrical systems, since almost all polyatomic molecules do have electronic states, which are close in energy\(^{†}\).[70]

\(^*\)formally evaluated by direct product of the electronic states \( \Psi_0 \otimes \Psi_n \)

\(^{†}\)consider also the concept of pseudo-symmetry[71]
3.1.2 Orbital Vibronic Coupling for DFT

The use of DFT implies the standard Born-Oppenheimer approximation, which neglects vibronic coupling. However, symmetry induced orbital mixing raised by the linear combination of atomic orbitals (LCAO) can result in the formation of new covalence in a low symmetry configuration. This process is closely related to the PJT stabilization and illustrated by orbital vibronic coupling.\[^{[72]}\] When considering the potential energy operator of Eq. (3.1) as a sum of separate electron-nuclear Coulomb interactions $V(r, Q) = \sum_k V_k(r_k)$, the linear vibronic coupling matrix reduces to the form of one-electron excitations into the virtual MOs $F_Q = \langle \phi_i \left| \frac{\partial V}{\partial Q} \right| \phi_j \rangle$, (3.3)

where the wave functions $\Psi$ of Eq. (3.2) are replaced by molecular orbitals $\phi$. Note, any one-electron excitation can contribute to a PJT instability if the vibration energy of the normal mode is $\hbar\omega_Q \gg |E_j - E_i| = \Delta_{i,j}$ (adiabatic condition). Computing the oscillator strength of such a single-electron transition by TD-DFT provides a valuable indicator of a present PJT coupling.\[^{[73]}\]

3.1.3 Pseudo Jahn-Teller Distortion of $\lambda^3$-Iodane Systems

Given its 10 valence electron configuration, trigonal planar IH$_3$, if distorted along an $e'$ normal mode, will take a T-shape structure which is lower in energy. From Figure 3.2 it is apparent that the degenerate LUMO splits into a $2b_2$ and a $4a_1$ component. The latter will interact with the $3a_1$ HOMO, leading to its stabilization. An other effect of this orbital mixing is the localization of the canonical molecular orbitals (CMOs) along the 3-center and the 2-center bonds, respectively. This implies a shift of s-character from the original $a'_1$ HOMO to the new $a_1$ LUMO. When localized, these frontier orbitals take the perfect shape of the 3c-4e bond orbitals (Figure 3.2 rhs).

The resulting PES is usually described as a “wrapped mexican hat” potential\[^{[70]}\] with the D$_{3h}$ structure, a second order saddle point, in its center. In this configuration, for IH$_3$, the lowest allowed excited state is indeed of $^1E'$ symmetry, dominated by the contribution of the $a'_1 \rightarrow e'$ HOMO-LUMO transition. Located
around the center of the PES, three minima are interconnected by isomerization transition states.‡ The relevant two degenerate normal modes of \( \epsilon' \) symmetry are coupling the electronic ground state \( ^1\Lambda' \) with the excited state state \( ^1E' \), resulting in a distortion along one \( \epsilon' \) bending mode \( ^1\Lambda' \otimes ^1E' = \epsilon' \). PJT effects have also been observed in computational studies on halogen trifluorides (\( \text{XF}_3 \)).[73–75]

Furthermore, a large oscillatory strength is additionally observed, indicating a coupling to the high lying virtual \( d_{x^2-y^2} \) orbital. Like the HOMO, it transforms from \( \epsilon' \) symmetry to \( a_1 \) upon distortion. Even though the energy gap is considerably large, vibronic coupling might elevate this interaction to an

‡In the PES of \( \text{IH}_3 \) the isomerization TS is also a second order saddle point, which is in contrast to \( \text{IF}_3 \) and presumably also to differently substituted \( \lambda^3 \)-halides. Nevertheless, for the sake of clarity we will not discuss this issue here.

---

**Figure 3.2:** Stabilization of the symmetry broken configuration of \( \text{IH}_3 \) caused by vibronic coupling with an excited state or Pseudo Jahn-Teller (PJT) effect, respectively. The symmetry induced mixing in the new configuration shifts the s-character from the 2-center into the 3-center axis. This directed decomposing is emphasized in the 3c-4e bond model (compare localized orbitals on the right side).

**Figure 3.3:** The largest oscillatory strength in \( \text{IH}_3 \) is observed for the displayed localized virtual NLMO corresponding to a \( d_{x^2-y^2} \)-orbital.
3.1 \( \lambda^3 \)-IODANES AND THE PSEUDO JAHN-TELLER EFFECT

important contribution to the stability of \( \lambda^3 \)-iodines (d-orbital back-bonding\(^3\)). As a matter of fact, this orbital appears to localize along the 3-center axis forming a \( d_{z^2} \)-like orbital with the right symmetry to mix into \( 3c_b n_b \) (see Figure 3.3).

3.1.4 THE ENERGY PENALTY OF PLANARITY VIOLATION

If, on the other hand, Y-shaped \( \text{IH}_3 \) is distorted along an \( a''_2 \) normal mode, leading to a non-planar geometry with \( C_{3v} \) symmetry, we again observe a PJT effect. In this case, however, the two highest occupied orbitals start mixing (Figure 3.4), leading to an overall destabilization. This illustrates the energy penalty for a planarity violation in situations where strain forces a non-planar transition state geometry. With regard to electronic structure, we observe that this distortion transforms the character of the HOMO from a non-bonding to an antibonding orbital, resulting in a destabilization of the HOMO by as much as 15 kcal/mol. In other words, the \( p_z \) lone pair \( 1a''_2 \) at the iodine center preserves the planarity of \( \text{IH}_3 \) and contributes to unfavorable orbital mixing in case of this out-of-plane distortion.

Figure 3.4: A distortion of the hydrogen ligands of \( \text{IH}_3 \) out of the molecular plane causes a strong destabilization, due to the unfavorable mixing in the pyramidal configuration involving the lone pair of the iodine center. The electron configuration of \( \text{IH}_3 \) is therefore responsible of the planarity retention of iodonanes.
Again, additional evidence for the presence of PJT-coupling is provided by inspecting single-electron transitions. In this case, the transition of interest involves the HOMO and the virtual $6p_z$ orbital (which has equal symmetry as the HOMO−1): $\alpha'_1 \rightarrow \alpha''_2$. Even though it contributes to a high-lying excited state, it marks the first allowed spin singlet. In the out-of-plane C$_{3v}$ configuration, the oscillator strength of this excitation increases significantly, pointing at an enhancement of the coupling to the $\alpha''_2$ bending mode.

### 3.2 ELECTRONIC STRUCTURE AND THE 3-CENTER-4-ELECTRON BOND MODEL

For a more general understanding of 3-center bonding in $\lambda^3$-iodanes in the framework of DAFH, it useful to examine model systems such as IH$_3$ and IF$_3$. Even though electronically these two model compounds represent two extremes, the CMOs show no fundamental difference in the bonding pattern. Nevertheless, the role of multicenter bonding appears to be quite different based on the DAFH analysis.

Table 3.1: QTAIM charges $\delta$ and DAFH occupation numbers $\eta^\Omega_i$ of the iodine domain $\Omega_I$ and the ligand domains $\Omega_{2cb/3cb}$ of the model systems, before and after localization (denoted as canonical and localized, respectively).

<table>
<thead>
<tr>
<th></th>
<th>$\delta_1$</th>
<th>$\delta_{3cb}$</th>
<th>$\delta_{2cb}$</th>
<th>$\Omega_I$</th>
<th>$\Omega_{2cb}$</th>
<th>$\Omega_{3cb}$</th>
<th>$\Omega_{3cb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IH$_3$</td>
<td>+0.80</td>
<td>-0.35</td>
<td>-0.10</td>
<td>1.05</td>
<td>1.06</td>
<td>0.24</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.04</td>
<td>1.06</td>
<td>0.25</td>
<td>1.27</td>
</tr>
<tr>
<td>IF$_3$</td>
<td>+1.90</td>
<td>-0.66</td>
<td>-0.58</td>
<td>0.53</td>
<td>0.49</td>
<td>0.09</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.49</td>
<td>0.31</td>
<td>0.31</td>
<td>1.67</td>
</tr>
</tbody>
</table>

In comparison to IH$_3$, all iodine DNOs of IF$_3$ show remarkably low occupation numbers by the reason of its very polar I–F bonds. As a matter of fact, the localization procedure appears to give a fundamentally different picture of the bonding.

---

5) i.e. we observe an electronic structure as shown in Figure 1.2a) for both compounds
3.2 ELECTRONIC STRUCTURE AND THE 3C-4E BOND MODEL

Figure 3.5: Bond DNOs of the iodine domain Ω₁ belonging to the T-shape configuration of the model systems IH₃ (a) and IF₃ (b), before and after localization.

pattern (Table 3.1). A weak response of the 3-center orbitals upon isopycnic transformation, on the other hand, implies that the multicenter nature of the DNOs is intrinsic. Obviously IH₃ represents a perfect model for the 3c-4e bond, as its orbitals are barely modified (see Table 3.1 and Figure 3.5). For IF₃, with its strongly electron-withdrawing ligands, we observe that the isopycnic transformation leads to two equivalent and perfectly localized 2-center bonding orbitals oriented along the 3-center axis. The two bonds are very polar and the corresponding occupation numbers ηᵪ indicate total absence of coupling (0.31 + 1.67 = 1.98 electrons per broken valence pair). At the same time, the broken valences of IH₃ only add up to close to four electrons, considering all of the 3-center DNOs (1.06 + 1.27 = 2.33 and 0.25 + 1.27 = 1.52 for the 3cb and 3cbⁿᵇ pair, respectively). Thus, by separately summing up the occupation numbers of the 3cb and 3cbⁿᵇ contributions, we can relate these observations directly to the 3c-4e picture.

These observations can be connected to the PJT effect, which is the driving force determining the geometrical arrangement of the ligands.[76] The starting point of the Jahn-Teller distortion is the D₃h high symmetry configuration with the ligand atoms arranged in trigonal fashion around the iodine center resulting in a Y-shape structure. By distortion towards a T-shape C₂ᵥ configuration, a symmetry induced orbital mixing is observed stabilizing the lower symmetry geometry (see Figure 3.2). The total stabilization amounts to 33.80kcal/mol in total energy for IH₃, much larger than the 11.17kcal/mol computed for IF₃. In fact, particularly the 3cbⁿᵇ orbital profits from increasing covalence, which manifests itself in the reduction of s-character by descending towards the T-shape.
configuration. For IF$_3$, the more pronounced hybridization defect of iodine leads to less PJT stabilization. At the same time, the isopycnic transformation results in three equivalent and very polar 2-center orbitals, while in IH$_3$ the bond DNOs are largely conserved (see Figure 3.6). In the end, IF$_3$ exhibits only a small change in the QTAIM charges of the fluorine atoms upon distortion, as electron-withdrawing ligands enforce localization of the iodine valence orbitals towards their own domain for both configurations. Actually, already the low population of 0.09 electrons of the canonical 3cb$^{nb}$ DNO of IF$_3$ refers to less pronounced multicenter bonding (Table 3.1), and the “decoupling” of the 3-center bonds is in stark contrast to the CMO picture.

### 3.3 RELATIVISTIC ASPECTS OF HYPERVALENT BONDING

The series of hypervalent compounds EF$_3$ (E=I, At, and element 117) became a popular array for the study of the impact of relativistic (scalar as well as spin-orbit coupling) and correlation effects on the structure of molecules containing heavy atoms.$^{[74,75]}$ For the research presented here, the fact that in IF$_3$ spin-orbit (SO) coupling effects are smaller than the effect of correlation is very important. Strong SO interactions would counteract the pseudo Jahn-Teller (PJT) distortion and stabilize the D$_{3h}$ configuration (as it is, in fact, the case for AtF$_3$.)$^{[75]}$ This view was confirmed by the two-component relativistic CCSD(T) calculations of van Wüllen and coworkers.$^{[77]}$
3.3 RELATIVISTIC ASPECTS OF HYPERVALENT BONDING

Table 3.2: Difference of the atomic or molecular orbital energy levels, respectively, relative to the relativistic spin-free calculation. Additionally listed are the results of the transition states of the isomerization (IH₃⁻) and the reductive elimination (IH₃⁰⁻) reactions.

<table>
<thead>
<tr>
<th>AO</th>
<th>I</th>
<th>IH₃⁻</th>
<th>IH₃⁻⁰⁻</th>
<th>IH₃⁰⁻ TS</th>
<th>MO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5s</td>
<td>+0.05</td>
<td>+0.23</td>
<td>+0.17</td>
<td>+0.23</td>
<td>s</td>
</tr>
<tr>
<td>5p 1/2</td>
<td>-16.51</td>
<td>-4.51</td>
<td>-6.69</td>
<td>-1.05</td>
<td>2cb</td>
</tr>
<tr>
<td>5p 3/2</td>
<td>+7.52</td>
<td>+3.01</td>
<td>+4.98</td>
<td>-0.94</td>
<td>3cb</td>
</tr>
<tr>
<td>5p 3/2,z</td>
<td>+7.52</td>
<td>+0.39</td>
<td>+0.28</td>
<td>+0.82</td>
<td>pₓ</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>+0.11</td>
<td>+0.13</td>
<td>+0.12</td>
<td>3cb nb</td>
</tr>
</tbody>
</table>

In order to get a qualitative picture of the influence of the SO interaction on chemical bonding, we will first study the energetic impact on the single-particle functions of atomic iodine and the model compound IH₃. In Table 3.2 the energy levels of the atomic and molecular orbitals are listed relative to the relativistic spin-free calculations of the iodine atom. The lowering of the energy level of 5p 1/2 results in a splitting of the 5p-orbitals of around 24 kcal/mol. Even so, the consequence for the molecular orbitals of the equilibrium geometry of IH₃ is moderate and in the same range for its transition states (see Table 3.2). Yet a larger effect is to be expected on the spatial extent of the spinors.

Figure 3.7: Orbital densities of relativistic MOs of IH₃ at an isovalue of 0.025.

In contrast to non-relativistic orbitals, Dirac spinors cannot be easily visualized. One way is to plot their density, as presented for IH₃ in Figure 3.7. With exception of a minor symmetry-forbidden admixture in the 3cb orbital density, hardly any deviations to the non-relativistic picture is seen (at the given

---

Footnote: This is rather moderate comparing to Astatine with a 6p-splitting of 71 kcal/mol.
Thus, the non-negligible splitting of the p-shell seems to have little influence on the bonding pattern. Even if the lowering of the \( p_{1/2} \)-AO enhances anti-bonding character in \( 2c_b^* \), the symmetry induced mixing with that virtual orbital amounts to a very similar PJT stabilization of \( 33.89 \text{kcal/mol} \). A more detailed analysis of the atomic orbital contributions to the corresponding orbitals confirms indeed this view in large parts (see Table 3.3). Anyway, closer inspection of the Gross populations obtained by Projection analysis reveals significant contributions of all p-orbitals in each bond orbitals. In particular, the \( p_{3/2} \)-admixture into the \( 3c_b^{nb} \) orbital introduces anti-bonding character, but still with minor consequences to the PJT stabilization. These observations also account for IF\(_3\), as shown in Table 3.4.

Table 3.3: Molecular orbital decomposition into atomic valence contributions IH\(_3\) obtained by Projection analysis. The atomic basis of iodine was increased by 6s, 6p and 5d functions to complete the reference set.

<table>
<thead>
<tr>
<th>EV</th>
<th>MO</th>
<th>I 5s</th>
<th>I 5p(_{1/2})</th>
<th>I 5p(_{3/2})</th>
<th>I 5p(_{3/2,z})</th>
<th>H(_2c_b) 1s</th>
<th>H(_3c_b) 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.7636</td>
<td>s</td>
<td>0.84</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>-0.4423</td>
<td>2c_b</td>
<td>0.30</td>
<td>0.56</td>
<td>0.23</td>
<td>0.16</td>
<td>0.47</td>
<td>0.19</td>
</tr>
<tr>
<td>-0.4219</td>
<td>3c_b</td>
<td>0.20</td>
<td>0.13</td>
<td>0.47</td>
<td>0.33</td>
<td>0.33</td>
<td>0.31</td>
</tr>
<tr>
<td>-0.3159</td>
<td>p_z</td>
<td>0.04</td>
<td>0.54</td>
<td>0.40</td>
<td>0.71</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>-0.2170</td>
<td>3c_b(_{nb})</td>
<td>0.35</td>
<td>0.13</td>
<td>0.21</td>
<td>0.02</td>
<td>0.31</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 3.4: Molecular orbital decomposition of IF\(_3\) obtained by Projection analysis. The atomic basis of iodine was increased by 6s, 6p, 5d and 4f functions, as well as 3s and 3p functions for fluorine to complete the reference set.

<table>
<thead>
<tr>
<th>EV</th>
<th>MO</th>
<th>I 5s</th>
<th>I 5p(_{1/2})</th>
<th>I 5p(_{3/2})</th>
<th>I 5p(_{3/2,z})</th>
<th>F(_2c_b) 2p</th>
<th>F(_3c_b) 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.7823</td>
<td>s</td>
<td>0.91</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.45</td>
<td>0.21</td>
</tr>
<tr>
<td>-0.5411</td>
<td>2c_b</td>
<td>0.13</td>
<td>0.48</td>
<td>0.08</td>
<td>0.21</td>
<td>0.45</td>
<td>0.21</td>
</tr>
<tr>
<td>-0.5307</td>
<td>3c_b</td>
<td>0.16</td>
<td>0.05</td>
<td>0.43</td>
<td>0.22</td>
<td>0.35</td>
<td>0.04</td>
</tr>
<tr>
<td>-0.3907</td>
<td>3c_b(_{nb})</td>
<td>0.38</td>
<td>0.14</td>
<td>0.16</td>
<td>0.02</td>
<td>0.10</td>
<td>0.39</td>
</tr>
<tr>
<td>-0.3116</td>
<td>p_z</td>
<td>0.06</td>
<td>0.59</td>
<td>0.34</td>
<td>0.61</td>
<td>0.20</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\( ^{11} \)a similar effect is observed by introducing an asymmetric coordination sphere, discussed in Section 3.4.
3.4 RELATIVISTIC ASPECTS OF HYPERVALENT BONDING

However, as already discussed in Section 3.2, the two model systems IH₃ and IF₃ show a greater difference in bonding than visible in the picture of canonical molecular orbitals. This is reflected in the change of the iodine contact density ρₐ and its atomic contributions (Table 3.5). For illustration, the compounds IFₙ (n = 1, 3, 5, 7) are also included in Table 3.5 in order to show the impact on the contact density by gradually increasing the coordination number. The observed increase of the iodine contact density along the series IFₙ (n = 1, 3, 5) is due to the contraction of the s-valence shell by the polar I–F bonds. For bonding in IH₃, the incorporation of the 5s-orbital, on the other hand, has to be attributed to the covalent bonding of the hydrogen ligands. As consequence, the 5s-AO of iodine become effectively depopulated, which is also reflected in the iodine valence configuration listed in Table 3.6. As a matter of fact, s-orbital participation also occurs in the highly coordinated IF₇, in which the s-valence shell is forced into bonding due to the already fully involved p-orbitals.

Table 3.5: Projection analysis of the iodine contact density ρ₀, relative to the ground state atom. The intra-atomic contributions of iodine are split into principal moment (pm), containing core and valence contributions, and hybridization.

<table>
<thead>
<tr>
<th></th>
<th>IH₃</th>
<th>IF</th>
<th>IF₃</th>
<th>IF₅</th>
<th>IF₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-2.73</td>
<td>0.66</td>
<td>6.11</td>
<td>8.24</td>
<td>-22.02</td>
</tr>
<tr>
<td>pm</td>
<td>6.24</td>
<td>3.11</td>
<td>14.89</td>
<td>28.22</td>
<td>-24.73</td>
</tr>
<tr>
<td>core</td>
<td>11.53</td>
<td>0.55</td>
<td>2.91</td>
<td>7.35</td>
<td>1.72</td>
</tr>
<tr>
<td>5s</td>
<td>-5.02</td>
<td>2.43</td>
<td>12.29</td>
<td>21.80</td>
<td>-25.45</td>
</tr>
<tr>
<td>5p</td>
<td>-0.52</td>
<td>0.13</td>
<td>-0.37</td>
<td>-1.07</td>
<td>-1.17</td>
</tr>
<tr>
<td>hybrid</td>
<td>-8.97</td>
<td>-2.47</td>
<td>-8.79</td>
<td>-19.98</td>
<td>2.71</td>
</tr>
<tr>
<td>Interatomic</td>
<td>0.03</td>
<td>-0.05</td>
<td>-0.20</td>
<td>-0.40</td>
<td>-0.21</td>
</tr>
<tr>
<td>Polarization</td>
<td>2.48</td>
<td>0.00</td>
<td>2.78</td>
<td>5.18</td>
<td>4.48</td>
</tr>
<tr>
<td>Total</td>
<td>0.21</td>
<td>1.03</td>
<td>8.09</td>
<td>13.45</td>
<td>-17.32</td>
</tr>
</tbody>
</table>

In the end, the discussed aspects of relativistic bonding result in a very similar picture with respect to the non-relativistic analysis. The atomic contributions of the iodine contact density further account for the occurrence of hybridization defects in polar hypervalent iodanes: the 5s-shell contracts due to a deshielding effect of the 5p-orbital depopulation, which is a consequence of multicenter bonding.
Table 3.6: Partial charges $Q$ (upper part) of iodine and of two of the hydrogen/fluorine ligands (axial and equatorial), as well as the iodine valence configuration (lower part), both obtained by projection analysis (Gross population).

<table>
<thead>
<tr>
<th></th>
<th>$I$</th>
<th>$H/F_{ax}$</th>
<th>$H/F_{eq}$</th>
<th>$I_{5s}$</th>
<th>$I_{5p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$</td>
<td>0.62</td>
<td>-0.10</td>
<td>-0.25</td>
<td>1.82</td>
<td>4.26</td>
</tr>
<tr>
<td>$I_{5s}$</td>
<td>0.23</td>
<td>-0.22</td>
<td>-0.28</td>
<td>1.99</td>
<td>4.59</td>
</tr>
<tr>
<td>$I_{5p}$</td>
<td>0.74</td>
<td>-0.15</td>
<td>-0.20</td>
<td>1.99</td>
<td>3.49</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>-0.08</td>
<td>-0.12</td>
<td>1.95</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>0.76</td>
<td>-0.04</td>
<td>-0.12</td>
<td>1.57</td>
<td>2.45</td>
</tr>
</tbody>
</table>

3.4 MULTICENTER BONDING IN DIARYLIODANES

In general, only $\lambda^3$-iodanes with at least one aromatic group have sufficient stability to be experimentally isolated.$[^2]$ Hence, the most commonly used compounds are diaryliodanes derived from iodonium salts.$[^{17}]$ In this section, we investigate a representative series of 4-methoxyaryl-phenyl-iodanes (Figure 1.1b). The 4-methoxyaryl ligand is often used as directing group, governing the selectivity of the reductive elimination reaction. Here, the goal is to establish a relationship between 3-center bonding and the structural parameters. Therefore, the series of the iodane compounds is such that it covers a broad spectrum of substituents $X$ (Figure 1.1b). The most important results of the DAFH analysis, as well as the barriers of the reductive elimination and the isomerization reactions ($\Delta G_{\text{red.}}^\circ$ and $\Delta G_{\text{isom.}}^\circ$), are listed in Table 4.3.

Concerning general trends, we start by visual inspection of the iodine bond DNOs. For illustration, the 3cb and 3cb$^{nb}$ orbitals of two representative compounds are depicted in Figure 3.8. The response to a localization procedure
Table 3.7: Series of 4-methoxyaryl-phenyl-iodanes: given are the reaction barriers of the isomerization \( \Delta G_{\text{isom.}}^o \) and the reductive elimination \( \Delta G_{\text{red.}}^o \); the AIM charges \( \delta \) and DAFH occupation numbers \( \eta_i^\Omega \) of the different domains after localization. The domain are labeled as follows: iodine \( \Omega_I \), substituent \( \Omega_X \), 3-center carbon ipso-atom \( \Omega_{C_{aryl}} \), 2-center carbon ipso-atom \( \Omega_{C_{phenyl}} \). In addition, we summed up the associated broken valence pairs \( \sum \).

<table>
<thead>
<tr>
<th>( X )</th>
<th>( \Delta G_{\text{isom.}}^o )</th>
<th>( \Delta G_{\text{red.}}^o )</th>
<th>( \delta_I )</th>
<th>( 2\text{cb} )</th>
<th>( 3\text{cb} )</th>
<th>( 3\text{cb}^{n\text{b}} )</th>
<th>( \delta_X )</th>
<th>( 3\text{cb}^{n\text{b}} )</th>
<th>( \delta_C )</th>
<th>( 3\text{cb} )</th>
<th>( \delta_C )</th>
<th>( 2\text{cb} )</th>
<th>( \sum )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPh(_3)</td>
<td>21.03</td>
<td>21.09</td>
<td>0.74</td>
<td>1.08</td>
<td>0.99</td>
<td>0.21</td>
<td>-0.26</td>
<td>1.35</td>
<td>-0.26</td>
<td>1.35</td>
<td>-0.26</td>
<td>0.97</td>
<td>2.34</td>
</tr>
<tr>
<td>Ph</td>
<td>21.16</td>
<td>21.35</td>
<td>0.74</td>
<td>1.08</td>
<td>0.99</td>
<td>0.21</td>
<td>-0.27</td>
<td>1.36</td>
<td>-0.26</td>
<td>1.34</td>
<td>-0.26</td>
<td>0.97</td>
<td>2.33</td>
</tr>
<tr>
<td>Me</td>
<td>19.39</td>
<td>19.96</td>
<td>0.71</td>
<td>1.07</td>
<td>1.02</td>
<td>0.22</td>
<td>-0.24</td>
<td>1.22</td>
<td>-0.26</td>
<td>1.36</td>
<td>-0.26</td>
<td>1.05</td>
<td>2.38</td>
</tr>
<tr>
<td>N(_3)</td>
<td>10.96</td>
<td>15.26</td>
<td>0.81</td>
<td>1.10</td>
<td>0.94</td>
<td>0.14</td>
<td>-0.37</td>
<td>1.27</td>
<td>-0.29</td>
<td>1.18</td>
<td>-0.28</td>
<td>0.88</td>
<td>2.12</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>15.61</td>
<td>18.58</td>
<td>0.80</td>
<td>1.10</td>
<td>0.92</td>
<td>0.19</td>
<td>-1.11</td>
<td>1.49</td>
<td>-0.27</td>
<td>1.32</td>
<td>-0.28</td>
<td>0.90</td>
<td>2.24</td>
</tr>
<tr>
<td>OH</td>
<td>15.61</td>
<td>19.10</td>
<td>0.89</td>
<td>1.08</td>
<td>0.86</td>
<td>0.16</td>
<td>-1.17</td>
<td>1.65</td>
<td>-0.30</td>
<td>1.29</td>
<td>-0.25</td>
<td>0.92</td>
<td>2.15</td>
</tr>
<tr>
<td>F</td>
<td>16.90</td>
<td>20.62</td>
<td>0.94</td>
<td>1.08</td>
<td>0.85</td>
<td>0.12</td>
<td>-0.76</td>
<td>1.76</td>
<td>-0.30</td>
<td>1.23</td>
<td>-0.29</td>
<td>0.89</td>
<td>2.08</td>
</tr>
<tr>
<td>PMe(_2)</td>
<td>11.12</td>
<td>11.47</td>
<td>0.57</td>
<td>1.07</td>
<td>1.14</td>
<td>0.22</td>
<td>0.76</td>
<td>1.07</td>
<td>-0.25</td>
<td>1.33</td>
<td>-0.25</td>
<td>0.99</td>
<td>2.47</td>
</tr>
<tr>
<td>SPh</td>
<td>11.35</td>
<td>16.49</td>
<td>0.70</td>
<td>1.09</td>
<td>1.00</td>
<td>0.18</td>
<td>-0.35</td>
<td>1.44</td>
<td>-0.27</td>
<td>1.20</td>
<td>-0.27</td>
<td>0.92</td>
<td>2.21</td>
</tr>
<tr>
<td>Cl</td>
<td>10.88</td>
<td>19.45</td>
<td>0.78</td>
<td>1.11</td>
<td>0.95</td>
<td>0.14</td>
<td>-0.67</td>
<td>1.69</td>
<td>-0.29</td>
<td>1.17</td>
<td>-0.28</td>
<td>0.87</td>
<td>2.13</td>
</tr>
<tr>
<td>Br</td>
<td>9.52</td>
<td>18.85</td>
<td>0.71</td>
<td>1.13</td>
<td>0.99</td>
<td>0.14</td>
<td>-0.64</td>
<td>1.67</td>
<td>-0.28</td>
<td>1.15</td>
<td>-0.28</td>
<td>0.86</td>
<td>2.14</td>
</tr>
</tbody>
</table>

\( ^1 \) not a substituent (IPh\(_3\) = triphenyl iodane)
of these molecules is quite different. The shape of the bond orbitals of triphenyl iodane (Figure 3.8a) keeps significant delocalized 3c-4e bond character, while in bromo-4-methoxyaryl-phenyl-iodane the DNOs localize into separate 2-center bonds. To relate these observations to the 3c-4e picture, we need to separately sum up the occupation numbers $\eta_i^\Omega$ of the 3cb and $3cb^{nb}$ contributions (see last two columns in Table 3.7). If such a “broken valence pair” population deviates considerably from $\sum = 2$, the two electron pairs are considered as coupled. This is observed for almost all of the compounds presented. Only with strongly electron-withdrawing substituents the two pairs are nearly decoupled.

![Figure 3.8: Evolution of 3cb and 3cb^{nb} DNOs of the iodine domain for triphenyl-iodane (a) and bromo-4-methoxyaryl-phenyl-iodane (b) upon a localization procedure.](image)

Closer inspection of the isomerization barriers confirms that the most stable compounds of the series are iodanes coordinated by three aryl ligands. Focusing on the asymmetric diaryliodanes (e.g. $X = N_3$, NH$_2$, OH, F), a steady increase of $\Delta G^\circ_{\text{isom.}}$ is observed (see Table 3.7), however, at a lower level of stabilization. This trend goes along with the electron-withdrawing properties of these ligands. In fact, by breaking the symmetry of the 3-center bond, anti-bonding character interferes with the $3cb^{nb}$ orbital, which is in turn stabilized by the polarization of the hypervalent bonds (Figure 3.9). The symmetry breaking is also reflected in the contributions of the $s$ and $p_y$ basis functions in the relevant orbitals (see Table 3.8): only in the case of phenyl diaryliodane a total separation of $s$ and $p_y$ contribution occurs, avoiding the mixing of $3cb^{nb}$ and 3cb orbitals.
Table 3.8: Contributions of the $p_y$ and $s$ basis functions to the $3cb^{n,b}$ and $3cb$ iodine DNOs. In addition, the isomerization reaction barrier $\Delta G_{\text{isom.}}^\circ$ and the Pauling electronegativity (EN) of the ipso-ligand atoms X are shown for comparison.

<table>
<thead>
<tr>
<th>X</th>
<th>Ph</th>
<th>NH$_2$</th>
<th>OH</th>
<th>F</th>
<th>PMe$_2$</th>
<th>SPh</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_{\text{isom.}}^\circ$</td>
<td>21.16</td>
<td>14.01</td>
<td>15.63</td>
<td>16.90</td>
<td>14.30</td>
<td>10.92</td>
<td>10.88</td>
<td>9.52</td>
</tr>
<tr>
<td>$p_y$ in $3cb^{n,b}$</td>
<td>0.03</td>
<td>0.32</td>
<td>0.33</td>
<td>0.32</td>
<td>0.07</td>
<td>0.21</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td>$s$ in $3cb$</td>
<td>0.01</td>
<td>0.22</td>
<td>0.21</td>
<td>0.24</td>
<td>0.06</td>
<td>0.20</td>
<td>0.26</td>
<td>0.27</td>
</tr>
<tr>
<td>EN</td>
<td>2.55</td>
<td>3.04</td>
<td>3.44</td>
<td>3.90</td>
<td>2.19</td>
<td>2.58</td>
<td>3.16</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Figure 3.9: Impact of breaking the symmetrical ligand sphere in the $3cb^{n,b}$ (top) and $3cb$ (bottom) DNOs of $\lambda^3$-iodanes illustrated by varying the coordination in the 3-center axis: a) two equivalent ligands b) breaking the trans symmetry, but still having ligands of similar electro-negativity c) two significantly different ligands.

3.5 CONCLUSIONS

From the perspective of the canonical molecular orbital (CMO) model, multicenter bonding is present in virtually all hypervalent $\lambda^3$-iodane compounds. This model allowed to understand many structural and electronic features of these compounds based on molecular symmetry considerations. In the particular event of isomerization, the transition state is traversed via a Y-shape geometry. At the same time, a retention of planarity of the hypervalent region is beneficial in view of low reaction barriers. Both phenomena are related to a pseudo Jahn-Teller (PJT) effect.

Section 3.1.3 was structured to provide insight into the symmetry induced mixing by studying two model compounds IH$_3$ und IF$_3$. It was shown by the means of Domain Averaged Fermi Holes (DAFH) analysis that distortion to a low symmetry T-shape configuration is accompanied by a significant change in hybridization at the central iodine atom. The resulting stabilization gives rise to multicenter bonding and is most effective in symmetric $\lambda^3$-iodanes containing apolar ligands only.
Even though molecular symmetry and multicenter bonding account for the fundamental properties of these compounds, the analysis of DAFH presents a more detailed picture. It revealed that, on one hand, in electron-rich iodanes a distinct multicenter bonding is present, and that, on the other hand, electron-withdrawing ligands imply decoupling and localization of the two involved electron pairs. Based on these observations, it was possible to relate the multicenter picture with the reactivity of $\lambda^3$-iodanes.

In order to identify possible shortcomings of our conceptual considerations without a fully relativistic molecular description, efforts were also directed towards evaluation of spin-orbit (SO) coupling. Projection analysis of the iodine contact density based on relativistic atomic orbitals emphasized the role of hybridization defects: in the case $\lambda^3$-iodanes, polar ligands induce considerable contraction of the 5s-valence shell, by the reason of a deshielding effect that is the depopulation of the 5p-orbital. The influence of SO interactions on chemical bonding, on the other hand, plays only a minor part, and there is only a marginal mitigation of the PJT stabilization. In contrast to the non-relativistic picture, however, the $3\text{cb}^n\text{nb}$ is slightly disturbed by a $p_{3/2}$ admixture introducing antibonding character.
Reactivity of Hypervalent Iodine Reagents

There is violence inherent in any conception of reason.

Achille Mbembe

The hypervalent moiety of $\lambda^3$-iodanes takes a pivotal role in terms of reactivity and determines the versatile chemistry observed. These iodane reagents allow to carry out the reaction under mild conditions and, at the same time, allow for control of the selectivity of the reaction. It was highlighted in the previous Chapter 3 that the electronic configuration of $\lambda^3$-iodanes surrenders the reagents to be susceptible for a PJT effect. The consequence is the establishment of a 3-center-4-electron bond and, thus, the occurrence of nonequivalent bonds. This enables $\lambda^3$-iodanes to isomerize and react along unusual reaction patterns, in stark contrast to other hypervalent molecules, which are not affected by the PJT effect.

In this chapter, the main focus is directed towards clarifying the various mechanisms observed in reactions of $\lambda^3$-iodanes. First, we address the chemoselectivity of iodine guided functionalization reactions, which are subject to the chemistry of diaryliodonium salts (Section 4.1.1). The main focus, however, lies on reactive $\lambda^3$-iodane intermediates, from which competing reactions interfere in many ways (Section 4.1.2). Finally, a tentative reaction cycle for a transition metal-like chemistry of the Togni reagents is presented (Section 4.2).
Computational Details

The *ab initio* computations for this work were performed with the quantum chemical package *Gaussian 09* (G09 Rev A.02). All ground state geometries were optimized for closed shell singlet states by means of density functional theory (DFT). The B3LYP exchange-correlation functional was employed along with the aug-cc-pVDZ-PP basis sets. Scalar relativistic and scalar spin-orbit effects were considered for the iodine atom by use of a semi-local electron core potential, the Stuttgart-Koeln-MCDHF-RSC-28-ECP. Excited state energies were obtained by time dependent DFT with the same functional and basis sets. All energies are given as approximate Gibbs free energies at a temperature of 298.15K and standard conditions.

*For Section 4.1:*

Natural localized molecular orbitals (NLMOs) were obtained from the natural bond orbitals (NBOs) using the *NBO program version 3.1.*

*For Section 4.2.1:*

The molecular calculations of this section were obtained by DFT, using the quantum chemical package *Gaussian 09* (G09 Rev D.01), and Cartesian aug-cc-pVTZ-PP basis sets were employed. QTAIM partitioning of the electron density into atomic basins was performed with the *AIMALL (Version 14.04.17)* program suite. The QTAIM integrations in the presence of pseudopotentials were made possible by proper addition of core densities in the set of natural orbitals leading to the total density. The program for a posteriori analysis by the DAFH methodology was developed in house and is printed in full length in *Chapter A.*
4.1 THE CHEMISTRY OF
DIARYLIODONIUM SALTS

Diaryliodonium salts are versatile reagents for a number of arylation reactions.\cite{17} In the case of diaryliodonium salts containing two different aryl groups the selectivity issues arise as to which group will be transferred to a nucleophile (see Figure 4.1). In general, the selectivity of the reaction is determined by electronic effects, resulting in the functionalization of the less electron rich aryl group via reductive elimination. Apparently, the electron rich ligands play the role of directing groups and therefore govern the selectivity by means of electronic control.\cite{83} A further interesting and to some extent unique class of diaryliodonium salts are such having the two aryl groups either directly connected or bridged by a short alkyl chain, thus forming cyclic derivatives (see Section 4.1.2).\cite{84} We analyze herein the relation between structure and reactivity patterns of such compounds.

4.1.1 IODINE-GUIDED SELECTIVE ARYLATION

Various routes towards the synthetic potential of diaryliodonium salts were intensively visited by the application of different nucleophiles.\cite{17,85,86} The fact

![Figure 4.1: Conversion of a diaryliodonium salt with an azide resulting in the selective functionalization of the phenyl group via rapid isomerization of the iodane intermediates. All reaction products are the result of a reductive elimination.\cite{12}](image)
that different selectivities are observed for electronically similar ligands (see Scheme 4.1) indicates that steric effects also operate. DiMagno and co-workers suggested that steric hindrance will affect the transition state geometry and therefore determine the selectivity of the reaction. These authors also showed that electronic and steric effects can be combined to enhance selectivity of the reductive elimination reaction. By introducing sterically demanding aryl ligands, a unidirectional selectivity was achieved.

In principle, the T-shaped iodane structure, formed upon an addition of the nucleophile \( X^- \) to the diaryl iodonium salts, allowing for three configurations (see Scheme 4.2). However, closer inspection showed that only two isomers are of relevance, namely those with the nucleophile involved in the 3c-4e bond. In addition, an equilibrium between the two isomers will be established. From each of these an intramolecular ipso-attack of ligand \( X \) is possible leading to the reductive elimination of the corresponding functionalized arene (see Figure 4.2).

**Scheme 4.1**: Different selectivities for the conversion of electronically similar diaryl iodoniums with \( \text{Br}^- \).[87]

**Scheme 4.2**: Different selectivities for reductive elimination reactions. Syn and anti refers to the orientation of the nucleophile \( X^- \) with respect to the aryl directing group (carrying the \( R_1 \) group).

As an illustrative example, the calculated stationary points on the reaction
4.1 THE CHEMISTRY OF DIARYLIODONIUM SALTS

Table 4.1: Differences between computed barriers in kcal/mol compared to observed experimental selectivities for the functionalization of a phenyl group using different directing groups.

<table>
<thead>
<tr>
<th></th>
<th>X⁻</th>
<th>ΔΔ G‡ ¹) (anti:syn)</th>
<th>exp. ratio ²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(OCH₃)Ph</td>
<td>Br⁻</td>
<td>-2.05</td>
<td>9 : 1</td>
</tr>
<tr>
<td>o-tol</td>
<td>Br⁻</td>
<td>2.02</td>
<td>13.3 : 86.7</td>
</tr>
<tr>
<td>p-tol</td>
<td>Br⁻</td>
<td>-0.62</td>
<td>73.2 : 26.8</td>
</tr>
<tr>
<td>p-tol</td>
<td>N₃⁻</td>
<td>-0.79</td>
<td>65 : 24</td>
</tr>
<tr>
<td>SECURE</td>
<td>N₃⁻</td>
<td>-2.27</td>
<td>96 : 0</td>
</tr>
</tbody>
</table>

¹) negative values for the Gibbs free energy difference ΔΔG‡ indicate a lower barrier for the functionalization of the phenyl group
²) [2.2]paracyclophanyl; unlike to the other cases the experimental ratio corresponds to the functionalization of anisyl.

The selectivity predicted for this particular reaction is in fact in qualitative agreement with the experimental result. The computed barrier leading to the anti product is 2.05 kcal/mol lower in energy, showing that the anti product is favored over the syn product, which reflects with the experimental ratio of 9 : 1 (see Table 4.1). The selectivity found for this and similar reactions support the validity of the Curtin-Hammett principle: the computed barrier height for the dominant product is consistently lower than the one of the alternative product.
features are likely to influence the selectivity observed. We would therefore expect to see a difference in the 3c-4e bonds of the two reactive iodane isomers. Upon inspection of the partial charges of the ipso-atoms as obtained from a natural population analysis (see Section 4.5), one can compare the polarity of the 3c-4e bond of the syn and anti isomers. It is remarkable that the partial charge on the iodine center is always close to +1.0 and is compensated by the negative partial charges on the ligand ipso-atoms in the 3c-4e bond. This in line with the orbital picture presented in Figure 1.2.

Analyzing the example in Table 4.2 the result is \( \Delta \delta_I = +0.99 \) and \( \Delta \delta_{BR} = -0.61 \) in the syn as well as in the anti configuration. The relevant difference of the polarity of the 3c-4e bond lies therefore in the ipso-carbon atom of the aryl ligands (highlighted red in Table 4.2). Indeed the partial charge of the ipso-carbon atom of the anisyl directing group amounts to -0.35 electrons, i.e. it is 0.04 electrons more negative than the ipso-carbon atom of the phenyl ligand in the same position in the syn isomer (\( \Delta \delta_{ipso} \) in Table 4.2). At this point it is interesting to explore whether there is a correlation between the polarity of the 3c-4e bond and the outcome of the reductive elimination reaction.

In Figure 4.3 the partial charge differences between the ipso-carbon atoms

![Figure 4.3: Reaction profile of bromo-4-methoxyaryl-phenyl-iodane giving the relative barrier heights \( \Delta G^\ddagger \) and their absolute differences \( \Delta \Delta G^\ddagger \) expressed in terms of Gibbs free energies. Also included are the structures of the relevant stationary points.](image)
4.1 THE CHEMISTRY OF DIARYLIODONIONUM SALTS

Table 4.2: Natural charges of the ligand ipso-atoms $\delta_{ipso}$ in the syn and anti isomers of a series of diaryliodanes (with $X = N_3$, Br). One of the aryl ligands is a phenyl group present in all compounds and the other ligand is referred to as directing group. The highlighted atoms correspond to the aryl ipso-atoms involved in the 3c-4e bond.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta \delta_{ipso}(X=N_3)$</th>
<th>$\Delta \delta_{ipso}(X=Br)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(OCH$_3$)Ph</td>
<td>-0.04</td>
<td>-0.04</td>
</tr>
<tr>
<td>4-(NH$_2$)Ph</td>
<td>-0.04</td>
<td>-0.06</td>
</tr>
<tr>
<td>o-tol</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>m-tol</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>p-tol</td>
<td>-0.01</td>
<td>-0.02</td>
</tr>
<tr>
<td>4-(CF$_3$)Ph</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>4-(C$_3$H$_5$)Ph</td>
<td>-0.02</td>
<td>-0.02</td>
</tr>
<tr>
<td>mesyl</td>
<td>-0.02</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

1) negative values of $\Delta \delta_{ipso}$ indicate a dominating directing group
2) 4-cyclopropyl phenyl

$\Delta \delta_{ipso}$ is plotted against the corresponding $\Delta \Delta G^\ddagger$ value. The plot indeed reveals a relationship between these two parameters. The greater the difference between the partial charges of the two ipso-carbons, the more pronounced the selectivity. For negative $\Delta \delta_{ipso}$, the prediction is that the reaction leans towards the functionalization of the phenyl ligand, whereas the opposite is true for the few cases with a positive difference of the partial charges. The cases where the experimental selectivity is known, actually confirm these predictions. For the anisyl directing group, the example discussed above, the partial charge difference of 0.04 electron relates to a difference in the reductive elimination barrier of 2.05 kcal/mol, thus favoring the functionalization of the phenyl group, consistent with the experimental observations of a 9:1 ratio. Further, it is important to note that the polarity correlates with experimental Hammett $\sigma$-parameters,$^{[92]}$ associated with the directing group.

However, there are a number of cases that do not follow this pattern (empty diamonds in Figure 4.3). Closer inspection shows that these involve aryl ligands
with bulky substituents. In these cases steric hindrance plays a role resulting in functionalization of the directing group rather than the phenyl ligand. Apparently, the barrier for the functionalization of the mesyl group is lower than the one for the phenyl. Figure 4.3 can be divided into $2 \times 2$ sectors, namely two sectors containing cases where the outcome of the reaction appears to be controlled by the 3c-4e bond polarity, i.e. phenyl functionalization along with negative charge differences, and directing group functionalization with positive charge differences. The two off-diagonal sectors show cases where other effects determine the selectivity. Obviously, in the case of small or zero polarity difference electronic control is absent, and the outcome of the reaction is determined by different factors. This was later demonstrated and confirmed experimentally by other groups.\[93\]

4.1.2 BRIDGED DIARYLIODANES

A further interesting and to some extent unique class of diaryliodonium salts are such having the two aryl groups either directly connected or bridged by a
short alkyl chain, thus forming cyclic derivatives (see Scheme 4.3). The heterocycle can be viewed as consisting of a iodine center bearing bridged ligands. Even though this heterocycle shows no aromaticity, bridged diaryliodonium ions are poorly reactive. Considering the conversion with the same nucleophile under similar conditions, the ring systems tend to undergo a radical reaction (Scheme 4.3), rather than a reductive elimination reaction as observed for unbridged compounds in the previous Section 4.1.1. However, with increasing ring size of the heterocycle, the observed reactivity becomes more and more equal to the one of the corresponding unbridged systems.

Scheme 4.3: Diaryliodonium salts with bridged ligands (1,1'-biphenyl iodonium) convert to different products depending on the reaction conditions. The RE leads to functionalization as well as arene coupling products. In addition, also products of radical reactions are observed.

Grushin proposed that conformational nonrigidity is the key factor determining the difference in reactivity. He also presented a tentative mechanistic explanation to account for the experimental observations. Accordingly, the conversion of bridged diaryliodonium salts with nucleophiles first leads to the formation of a T-shaped hypervalent iodine intermediate, which is able to isomerize to a higher energy Y-shaped geometry (see Scheme 4.4). In order to follow a symmetry-allowed mechanism, the subsequent reductive elimination reaction has to start from such a Y-shaped configuration. Consequently, the reaction outcome depends on the accessibility of the Y-isomer, which is again dependent on the size of the heterocycle. The reactivity would therefore be determined by the heights of the isomerization and the homolytic decomposition barriers.

As long as no bulky arene ligands are involved, the reaction of a diaryliodo-
Scheme 4.4: The RE reaction involving bridged diaryliodonium salts as proposed by Grushin.[84]

Scheme 4.5: Illustration of the planarity retention of the hypervalent region in the course of the reaction shown in Figure 4.1. The plane (in yellow) is defined by the three ipso-atoms coordinated to the iodine center. Displayed are the geometries of the isomerization TS, of the intermediate (equilibrium) and of the TS of a RE reaction.

Thanks to their rigid geometry, bridged diaryliodanes, on the other hand, are suited systems to study the impact of a forced deviation from planarity of
the hypervalent region. The bridge between the aryl ligands restricts certain degrees of freedom for the possible reaction pathways. Obviously, being the ring size a tunable parameter, this restriction will vary with the size of the bridge. Figure 4.5 depicts the calculated stationary points of the reaction pathways of the 5-membered ring system, starting from a bromo bisphenyl iodane intermediate formed in-situ, as a specific example. Figure 4.5 shows that in contrast to most unbridged iodanes, the elimination of the original iodonium ligands becomes accessible. The product of interest in this case is biphenylene, which is denoted in the following as the "arene coupling" product in order to distinguish it from the functionalization product. Besides the two reductive elimination reactions the iodane intermediate is able to isomerize and to react via a competitive radical process (see Section 4.4).

![Figure 4.5](image)

**Figure 4.5:** Possible reaction pathways starting from the hypervalent intermediate bromo 1,1'-biphenyl iodane. The preference for a certain reaction pathway depends on the reaction conditions as well as on the bridge size. Obviously, the iodane intermediate is acting as the "gateway" for all reactions.

From Figure 4.5 it is apparent that both transition-state geometries for the reductive elimination reactions strongly deviate from the essentially planar structure of the intermediate. This is evidently a consequence of the strained ring system, which makes the intramolecular approach to the ipso-carbon more difficult. The result is an energy penalty for the corresponding reaction barriers. The computations further confirmed that decreasing the strain in the system by enlarging the ring size has a considerable effect on the barriers of the reductive elimination reactions (see Table 4.3). This is in agreement with the experimental
Table 4.3: Barriers of the competing reaction pathways (in kcal/mol) of a series of bridged diaryliodanes as a function of the bridge size $n$.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$n$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>no bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_3$</td>
<td>isom.</td>
<td>14.0</td>
<td>11.6</td>
<td>11.5</td>
<td>10.1</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>func.</td>
<td>29.4</td>
<td>22.5</td>
<td>18.0</td>
<td>14.5</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>coupl.</td>
<td>47.7</td>
<td>27.2</td>
<td>19.7</td>
<td>21.1</td>
<td>29.2</td>
</tr>
<tr>
<td>Br</td>
<td>isom.</td>
<td>13.8</td>
<td>10.9</td>
<td>10.6</td>
<td>9.6</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>func.</td>
<td>33.3</td>
<td>26.3</td>
<td>21.2</td>
<td>18.1</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>coupl.</td>
<td>48.9</td>
<td>27.4</td>
<td>19.6</td>
<td>21.3</td>
<td>28.6</td>
</tr>
<tr>
<td>Ph</td>
<td>isom.</td>
<td>29.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>func.</td>
<td>56.0</td>
<td>40.7</td>
<td>34.0</td>
<td>25.4</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>coupl.</td>
<td>30.8</td>
<td>21.2</td>
<td>18.7</td>
<td>17.6</td>
<td>21.4</td>
</tr>
<tr>
<td>PFP</td>
<td>isom.</td>
<td>21.1</td>
<td>16.8</td>
<td>17.6</td>
<td>15.3</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>func.</td>
<td>37.4</td>
<td>31.2</td>
<td>29.1</td>
<td>25.1</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>coupl.</td>
<td>36.3</td>
<td>23.2</td>
<td>19.5</td>
<td>19.5</td>
<td>24.2</td>
</tr>
</tbody>
</table>

1) pentafluorophenyl

Figure 4.6: a) Reaction barriers of the bromo diaryliodane series. Remarkably, the arene coupling has a minimum at the bridge size of $n = 2$ and is favored over the functionalization as well (compare also to Table 4.3). b) Out-of-plane angle $\alpha$ in the TS of the functionalization reaction of the same series.
4.1 THE CHEMISTRY OF DIARYLIODONIUM SALTS

observations reported by Grushin.[84]

Figure 4.6a shows the barriers for the three reactions – isomerization, functionalization, i.e. aryl-nucleophile coupling, and aryl-aryl coupling – of bridged bromo diaryliodanes as function of the bridge size. Evidently, the isomerization reaction (grey line in Figure 4.6a) is not much influenced by the ring size. On the other hand, the barriers of the reductive elimination reactions respond strongly to the ring size (blue and red lines Figure 4.6a). First, the functionalization barrier (blue line) steadily decreases from over 30 to less than 20 kcal/mol for large bridge sizes. Second, the arene coupling reaction is competitive only for ring sizes 6–8 (or bridge size n = 1–3), from where its barrier will increase again. This explains why the arene coupling reaction is usually not observed in reactions involving unbridged diaryliodanes.

The above-mentioned deviation from co-planarity of the iodine atom and its immediate bonding partners in the transition state may be defined by the angle α between the I–X vector and the plane containing the iodine atom and its two carbon bonding partners. As shown in Figure 4.6b this angle steadily diminishes from almost 80° in the case where the aryl groups are directly connected to each other (bridge size 0) to 0° in the case of an acyclic derivative. It is also clear that the activation barrier for functionalization correlates with this angle, i.e. the larger α, the higher the functionalization barrier. Apparently, the force, which is arises due to a plt effect, directs the reaction through a planar pathway as long as sterically possible (Section 3.1.3).

In contrast, the arene coupling reaction is not so clearly dependent from geometrical features. There is, however, experimental evidence for a slight

![Figure 4.7: The boat-type TS geometry of the arene coupling reaction of bridged (n = 2) bromo diaryliodane (compare δG and α values in Figure 4.6a).](image)
preference of the arene coupling reaction in the case of a 7-membered ring.\cite{84}

The calculations show that in this particular case, the striking difference lies in a
boat-like conformation of the transition state, which is readily accessible for a
7-membered ring structure (see Figure 4.7). However, the arene coupling process
appears to be feasible only if the equilibrium structure is already disturbed by
strain (Section 4.1.4).

### 4.1.3 Reductive Elimination Reaction:
Mechanistic Considerations

In order to obtain insight into the details of the reaction processes, we use the
concepts established by the exploration of the model systems in Chapter 3. The
application of the 3-center-4-electron bond model has already proven to be a
helpful tool to describe the reactivity of $\lambda^3$-iodane chemistry in a conceptual
framework (Section 4.1.1). For this part, the relevant aspects of the electronic
structure of the different diaryliodanes will be expressed by means of a natural
bond orbital (NBO) analysis.

![Figure 4.8: Frontier NLMOs energies of the bridged phenyl diaryliodanes. Panel (a)
shows that the increase of the bridge size $n$ has no substantial impact on the electronic
structure of the equilibrium geometries. This is obviously not the case for the transition
states of both RE reactions (b & c), where the orbital energies change significantly.](image)

In Figure 4.8 the energies of the frontier localized natural molecular orbitals
(LNMOs) of the bridged phenyl diaryliodanes are depicted as function of bridge
size $n$. The orbitals are labeled as 2-center (2cb) and 3-center (3cb) bonds of
bonding, non-bonding (nb) or anti-bonding (*) character. Both RE transition
states show noticeable variations of the orbital energies in response to ring size.
4.1 THE CHEMISTRY OF DIARYLIODONIUM SALTS

In stark contrast, the orbital energies of the equilibrium structures remain nearly constant.

From a conceptual point of view, the reductive elimination reaction can be considered as a heterolytic decomposition followed by an intramolecular nucleophilic attack. During the reaction, two bonds are broken and a new 2-center bond is formed, connecting the nucleophile and an aryl ligand (see Figure 4.9a). This context is illustrated in Figure 4.9 based on the reaction of bromodiaryliodane.

As most of the action involves the $3\text{cb}^{n\text{b}}$, the $3\text{cb}^*$ as well as the $2\text{cb}^*$ orbitals, the focus is kept on their evolution along the reaction coordinate. In the TS, the $3\text{cb}^{n\text{b}}$ HOMO gets polarized against the bromine ligand. The $3\text{cb}^*$ orbital, on the other hand, evolves in a complementary fashion: it is polarized on two centers, leaving no amplitude at bromine. Concomitantly, the empty $2\text{cb}^*$ is lowered in energy becoming the new LUMO. Hereon, the HOMO-LUMO interaction representing the intramolecular nucleophilic attack induces the breaking of the $2\text{cb}$ and the orbital recombination results in the new Br–Aryl bond (Figure 4.9b, r.h.s). To optimize the orbital interaction, the nucleophile may have to distort out-of-plane. This, however, is tied to an energy penalty.

Summarizing the results of this section, the RE is facilitated by an electron-withdrawing nucleophile which polarizes the 3-center bond, thus supporting the charge separation and hence the heterolytic decomposition.[12] The efficiency of the subsequent recombination step then essentially depends on the aryl ligand involved in the elimination.[93] This mechanism is valid for both types of RE reactions, but in the arene coupling the polarization of the $3\text{cb}^{n\text{b}}$ is unfavorable, as the reorganization of charge density is hindered by the trans ligand (i.e. the nucleophile), such as it is the case for the example shown in Figure 4.9b.

4.1.4 Reductive Elimination Reaction:
Symmetry Considerations

Exploring the RE reactions with the IH$_3$ model from an orbital symmetry perspective allows us to understand some additional mechanistic details (see also Section 3.1.3).[71,94] We have seen that both RE reactions, functionalization and arene coupling, are mechanistically similar, but display different transition state
Figure 4.9: a) Schematic representation of the RE reaction process of bromine diaryliodo-dane. b) The frontier LNMOs of bromine diaryliodane in the course of the RE reaction are displayed to show the evolution of the 3-center and the 2-center bond. In this process, the elimination of the most electron-withdrawing ligand is favored (here: bromine ligand). This process is supported by an initial charge separation (see strong polarization of $3\text{cb}^*_{\text{3cb}^*}$ in TS). The final recombination depends on the properties of the aryl ligands, as the $2\text{cb}^*$ becomes the acceptor orbital. The structure on the r.h.s is close to the TS and does not represent a stationary point.

Geometries. For functionalization reactions a bent TS geometry is observed, whereas a Y-shaped symmetric TS geometry is observed only in the case of arene coupling. This TS, however, has a higher barrier which appears to be incompatible with Grushin’s proposition, saying that all RE reactions have to pass through a Y-shape configuration in order to be symmetry allowed.

We address this issue with our model system by following the reactions starting from a T-shape ($C_{2v}$) and Y-shape ($D_{3h}$) configuration (Figure 4.10a). The orbitals and orbital energies shown are obtained from constrained scans along...
4.1 THE CHEMISTRY OF DIARYLLIODONIUM SALTS

**Figure 4.10:** a) Schematic representation of RE with IH$_3$. b) & c) Walsh diagrams of the elimination reaction of H$_2$ in the model system IH$_3$ starting from different configurations resulting in a symmetry forbidden (b) or a symmetry allowed reaction path (c). The orbitals are labeled according the C$_{2v}$ configuration and blue shaded orbital energies correspond to initially occupied orbitals. In addition, the evolution of the HOMO (3$\alpha_1$) and LUMO (4$\alpha_1$) is displayed along the reaction coordinates $\alpha$ and $\beta$.

The reaction coordinates of the two RE processes. In both cases, we imposed least deviation from the starting geometry, thus not strictly following the lowest energy pathway. For the elimination starting from the C$_{2v}$ configuration, a perpendicular arrangement of two of the ligands was imposed along the entire reaction coordinate. Analogously, the C$_2$-axis was chosen as constrain for the reaction pathway starting from the D$_{3h}$ configuration. Looking at the evolution of the CMOs, the striking fact is the crossing of an occupied and an unoccupied level observed for the RE starting from a C$_{2v}$ configuration (*Figure 4.10b*), indicating a symmetry forbidden reaction. On the other hand, starting from the Y-shape configuration, there is no crossing of occupied and empty levels, which would correspond to a symmetry allowed mechanism (*Figure 4.10c*). However, it should be noted that the D$_{3h}$ starting configuration† is much higher in energy and that, therefore, the reaction pathway is unlikely to pass through this Y-shape configuration.

It turns out that Grushin’s criterion of a Y-shape conformation is sufficient, but not necessary for a symmetry allowed reaction. In order for the RE reaction to take place anyhow symmetry allowed, the initial symmetry of the T-shape equilibrium structure has to be broken. The C$_{2v}$ ground state $^1A_1$ is brought into

†actually a saddle-point of IH$_3$ connecting the C$_{2v}$ configurations
correspondence with the product ground state $^3\text{B}_2$. As a matter of fact, inspection of the unconstrained reaction pathway reveals a deviation of the perpendicular arrangement resulting in an unsymmetrical bent Y-shape transition structure, but, still, the $\sigma_{xy}$-plane is preserved (Figure 4.11b). At the same time, an orbital level crossing is avoided. This bent geometry is found for the RE transition structures of $\lambda^3$-iodanes in general.

The direction of the functionalization reactions is actually determined by the electronic properties of the ligands, with electron-withdrawing ligands being preferably involved in the elimination process (Figure 4.11a). The situation changes if the less electron-withdrawing ligands are to be eliminated. In this case, much more energy is needed to overcome the reaction barrier. The most extreme situation is represented by the arene coupling reaction, in which the elimination of the corresponding ligands is such an unfavorable process that as much symmetry allowance as possible is incorporated. The result is a symmetrical TS geometry with a relatively high and therefore not competitive reaction barrier.

![Figure 4.11: Comparison of the RE TS structures of azo-4-methoxyaryl-phenyl-iodane (a) and IH$_3$ (b), both showing a bent Y-shape geometry. Note that the IH$_3$ TS structure is, unlike in Figure 4.10, from an unconstrained scan.](image)

### 4.2 ELECTROPHILIC TRIFLUOROMETHYLATION: THE TOGNI REAGENTS

The most challenging synthetic problem of transferring a trifluoromethyl group (CF$_3$) as an electrophile is to establish mild and selective reaction conditions. Hence, even though radical and nucleophilic strategies to introduce CF$_3$ already
proofed to be efficient synthetic methods, only a few reagents are capable of performing electrophilic trifluoromethylations. Togni and coworkers, however, developed a number of synthetic routes for the trifluoromethylation of a vast array of nucleophiles (see Figure 4.12). Some of these routes were opened only in the past few years.\[^{[1,18,95]}\] One example is the direct N-trifluoromethylation of azoles.\[^{[18]}\] Among the reagents developed by Togni et al., 3,3-dimethyl-1-(trifluoromethyl)-1\(\lambda^3\),2-benziodoxol (DMTB) (Figure 4.12b) can be considered as the “workhorse”.\[^{[1]}\] DMTB 1 is a stable dialkyliodane and is, thus, available off-the-shelf. It can be synthesized in a consecutive ligand exchange reaction at the iodine center.\[^{[1]}\] The use of Togni reagents allows for remarkably smooth and selective reactions. Activation with Lewis or Bronsted acids enables the reagents to increase significantly the range of application.\[^{[18,19]}\]

Besides the wide scope for synthetic applications, the trifluoromethylation reactions show a considerable mechanistic diversity, and breaking down the reaction cascades of e.g. N-trifluoromethylation provokes to be rather challenging. In this example, hypervalent iodine-guided reactions are used towards a series of variously substituted electron-rich N-heterocycles, i.e. imines and

---

**Figure 4.12:** The broad range of application for iodone-guided electrophilic trifluoromethylation with the Togni reagents (center): a) 3-oxo-1-(trifluoromethyl)-1,2-benziodoxole (OTB), and b) 3,3-dimethyl-1-(trifluoromethyl)-1\(\lambda^3\),2-benziodoxol (DMTB).\[^{[1]}\]
different kinds of azoles, such as indazoles, pyrazoles as well as tertrazoles. The 
N-trifluoromethylation is a very sensitive process for which substrate screening 
evoked an unexpected novel Ritter-type reaction under acid-catalyzed condi-
tions (Scheme 4.5).\[96] The following computational study aims to shed light on 
the mechanisms of competing reactions based on the established concepts of 
$\lambda^3$-iodane reactivity.

### 4.2.1 The Effect of Brønsted-Activation

Activation of DMTB is routinely performed by Brønsted acids, resulting in the 
protonation of the oxygen atom. This activation process has substantial impact 
on the nature of the 3-center-4-electron (3c-4e) bond, which is oriented along 
the O–I–C axis (shaded grey in Figure 1.1a). Already at the structural level, 
the protonation manifests itself by elongation of the O–I bond, suggesting a 
weakening of multicenter bonding (Scheme 4.6).\[97] In fact, the protonation of 
the oxygen atom of DMTB results in a new ordering of the CMOs (Figure 4.13). 
While in DMTB the LUMO corresponds to the anti-bonding character of the 
C$_{Ph-I}$ bond (2cb*), most contributions to the LUMO in the protonated form 
stem from the antibonding 3-center MO (3cb*). The pronounced polarization

---

**Scheme 4.5:** Formation of N-(trifluoromethyl-acetonitrile)imine 3 via a novel Ritter-type reaction.

**Scheme 4.6:** Activated form of DMTB ($1H^+$), protonated at the oxygen atom. The 
unsymmetrical weakening of the 3-center bond is indicated by the dashed line.
towards the I-CF$_3$ bond upon activation is indicating a significant weakening of
the 3c-4e bond.

\[ \text{Figure 4.13: Frontier CMOs of DMTB and DMTB-H}^{+} \text{ relative to their HOMO energies. The well localized CMOs (3cb$^{nb}$, 2cb$^*$ and 3cb$^*$) identify the region of hypervalent bonding. Upon protonation, the 3cb$^*$ is lowered significantly becoming the LUMO and having a pronounced polarization towards the I-CF$_3$ bond.}^{[1]} \]

In addition, the change in partial QTAIM charges along the 3-center axis further indicates a substantial modification in the electronic structure (see Table 4.4). Even though the protonation occurs at the oxygen atom, surprisingly, its partial charge is not affected. This is in contrast to the considerable change in polarization of the I–CF$_3$ bond. By comparing the magnitude of charges in Table 4.4 it is evident that the loss of negative charge in carbon atom of CF$_3$ is compensated by the gain of charge in the central atom. Obviously, the displacement of the oxygen atom from the 3-center axis influences the opposite bond, which is indirect evidence for delocalized bonding character as proposed in the 3c-4e bond model. This bonding pattern, as described by the canonical molecu-
lar orbitals (CMOs), is found in virtually all of these hypervalent compounds. It allows to explain the most important structure-bonding relationships.\cite{12,76} However, for the prediction of compound-specific features of the reactivity, the 3c-4e bond model is too general to consistently be a good descriptor. A more elaborate approach is required.

**Table 4.4**: QTAIM charges of the iodine center and the ligand ipso-atoms of DMTB before and after protonation.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMTB</td>
<td>0.96</td>
<td>-1.12</td>
<td>1.62</td>
</tr>
<tr>
<td>DMTB-H\textsuperscript{+}</td>
<td>0.74</td>
<td>-1.12</td>
<td>1.89</td>
</tr>
</tbody>
</table>

The reactivity of the Togni reagents depends on the characteristics of the hypervalent iodine center, which largely accounts for the unusual chemistry observed. To follow up the introductory arguments about the activation of these reagents, the domains belonging to the so-called hypervalent region are investigated (i.e. the domains of the central atom and of the ligand ipso-atoms). The results of the DAFH analysis of the Togni reagent is listed in Table 4.5, containing the occupation numbers of the valence DNOs of the iodine domain $\Omega_i$. Besides three broken valence orbitals, denoted as 3-center bonding (3cb), 3-center non-bonding (3cb\textsuperscript{nb}) and 2-center bonding (2cb) DNOs, there are also two lone pairs corresponding to the orbitals that resemble very much iodine s- and p\textsubscript{z}-orbitals (see Table 4.5 & Figure 4.14).

Visual inspection of the orbitals of the unprotonated compound reveals their delocalized character over 3-centers in the canonical form, but shows considerable localized bond orbitals after isopycnic transformation (Figure 4.14). While the 3cb\textsuperscript{nb} orbital is polarized strongly towards the oxygen atom after the localization procedure, the 3cb DNO still reaches into both ligand domains. The protonation amplifies the effect of having two separated 2-center bonds instead of delocalized 3-center bonding, meaning that the four electrons in the 3c-4e bond are now decoupled. This is also reflected in the evolution of the DNO of the oxygen domain participating in the 3-center bond. After protonation this DNO is not directed along the 3-center axis anymore.\cite{98} In essence, the oxygen DNO turns into a lone pair.
Table 4.5: Occupation numbers \( \eta_i \) of the valence DNOs belonging to the iodine domain \( \Omega_I \) of DMTB before and after protonation, with and without isopycnic localization. Obviously, the effect of the Brønsted-activation is larger than the change introduced by the localization procedure. The lowest population is actually observed in the 3cb\(^{n,b} \) orbital in accordance with the 3c-4e bond model.

<table>
<thead>
<tr>
<th>( \Omega_I )</th>
<th>canonical</th>
<th>localized</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s</td>
<td>p(_z)</td>
</tr>
<tr>
<td>DMTB</td>
<td>1.94</td>
<td>1.87</td>
</tr>
<tr>
<td>DMTB-H(^{\dagger +} )</td>
<td>1.96</td>
<td>1.89</td>
</tr>
<tr>
<td>OTB</td>
<td>1.95</td>
<td>1.87</td>
</tr>
<tr>
<td>OTB-H(^{\dagger +} )</td>
<td>1.96</td>
<td>1.88</td>
</tr>
</tbody>
</table>

The most substantial population change upon protonation is observed for the DNO with the shape of a 3cb orbital (see Table 4.5). Recalling the observations of the shift of partial charges, an analogous change in the polarization of the I–CF\(_3\) bond occurs, having a 3cb occupation number ratio of \( \eta_I : \eta_{CF_3} \) evolving from 0.79 : 1.23 before, to 1.00 : 0.98 after protonation. This change of polarization is accompanied by a substantial loss of population in the 3cb\(^{n,b} \) DNO (Table 4.4). Thus, the oxygen atom is not participating in the multicenter bond anymore. In such a case, DAFH analysis leads to an unambiguous picture of independent 3-center orbitals of DMTB-H\(^{\dagger +} \).

In comparison to the analysis of multicenter bonding in the diaryliodane...
series (see Section 3.4), the occupation numbers of the 3cb and 3cb$^{nb}$ of the Togni reagents appear to be overall smaller. This is actually an indication of a less stable hypervalent bonding. However, the two reagents do not behave exactly the same way upon activation. Besides the reported change of polarization, the protonation results only in the case of OTB in a complete decoupling of the 3-center broken valence pairs. Protonated DMTB-H$^{1+}$ has still a non-negligible contribution to delocalized 3-center bonding, which manifests in its marginally different reactivity (see Table 4.5). In the end, the activated Togni reagents are ready for capturing a nucleophile, performing the trifluoromethylation in a subsequent step.

### 4.2.2 Transition Metal Chemistry with Hypervalent Iodine

Scheme 4.7: Acid-catalyzed Ritter-type reaction: transition metal-like (left) and experimentally proposed (right) reaction cycles. During the reacion acetonitrile is a) captured in terms of an insertion reaction (see also Scheme 4.8), or b) N-trifluoromethylated and attacked subsequently by benzotriazole. The products of the two reaction cycle are identical (c & d).

Efforts towards the direct synthesis of electrophilically trifluoromethylated N-heterocycles using the DMTB reagent, resulted, under acid-catalyzed conditions in acetonitrile, into a novel Ritter-type reaction (see Scheme 4.5).\[96]\]

...
the N–CF$_3$ bond is formed by solvolysis and leads to a N-trifluoromethylated acetonitrilium ion, that is rapidly trapped by an azole nucleophile. The reaction is assumed to occur via reductive elimination of the trifluoremethyl group, however, early computational studies already challenged this mechanism (see Scheme 4.7)."[99] Unfortunately, there are no clear-cut experimental techniques beyond product studies for the consolidation of the experimental proposed reaction cycle. Therefore, additional theoretical investigations are promising to contribute towards a better understanding of the observed reactivity. Given the complexity of solvolysis reactions, these initial calculations are based on static quantum chemical methods in gas phase.

Quantum chemical exploration of the possible reaction pathways evoked a considerable mechanistic diversity, including reductive elimination (RE) and bimolecular nucleophilic substitution (SN$_2$) reaction steps (see Scheme 4.7). Following the course of the reaction cycle proposed by the experimentalists (EXP cycle) (Scheme 4.7b)[96] two competing reaction mechanism (RE & SN$_2$) are observed in silico. However, the reductive elimination can also lead to an other branch of the reaction cascade, which is reminiscent to a transition metal reaction cycle (TM cycle).

Activation of the reagent DMTB is required for both cycles. In order to follow up the arguments of the previous Section 4.2, we focused on the role of the 3-center-4-electron bond. In stark contrast to the mechanistic performance of diaryliodanes (see Section 3.4), DMTB is incapable (!) to isomerize into another configuration (compare Scheme 4.2). As a matter of fact, the reagent is subject to structural constrains by design. The fluxional properties of diaryl- or dialkyl-λ$^3$-iodane require flexibility of the most electron-withdrawing ligand, which corresponds the conformationally fixed oxygen atom in the case of the Togni reagents. Protonation at the oxygen ligand decouples the 3-center bond to a large extent (Section 4.2.1). However, by the reason of a “static solvent effect” (SSE), the protonated oxygen atom still exerts, albeit a significantly mitigated, structural constrain. As a result of the activation process, the coordination site at the central iodine atom is now also available for hard nucleophiles (see 1a in Scheme 4.7b). From a structure and bonding perspective, the activation process can be considered as a “switch” to alternate the orientation of the 3-center-4-electron bond.[99] This is necessary for the formation of a reactive complex.
1a, which is rather a $\lambda^3+1^-$ than a $\lambda^4$-iodane system, as the 3c-4e bond is now oriented along the C–I–N axis. In the end, this allows for only one way of elimination (Scheme 4.8).

Since the Ritter-type reaction represents a solvolysis, there is actually a significant probability towards coordination of MeCN.$^{[100]}$ When traversing a reaction pathway along the TM cycle, free acetonitrilium ions do not occur (see Scheme 4.7a). The reason is the possibility of an insertion reaction, which corresponds to an intra-molecular attack ($\Delta G = 39.4$ kcal/mol) followed by a 1,2-shift (Scheme 4.8b). This is a ligand exchange reaction of $1\text{H}^+$ and leads to a stable intermediate ($\Delta G = -2.1$ kcal/mol in reference to 1). When following now the EXP reaction pathway, a free trifluoromethyl-acetonitrilium 5 intermediate is formed right-away, that is then rapidly trapped by an azo nucleophile 2 (Scheme 4.7b & Scheme 4.8c). By the reason of identical transition states of the insertion and the RE reaction (Scheme 4.8a), the occurrence 1,2-shift, in fact, divides the reaction cycles into two branches. In order to discriminate the products 4 and 5 of the RE (Scheme 4.7 a & b), further efforts have to be directed towards the exploration of the so-called “valley-ridge inflection point” (VRI).$^{[101,102]}$ The requirement of such a mechanism is an orthogonal reaction coordinate, which connects the two products 4 and 5 of each cycle (see Scheme 4.7). This is the case, if the least motion pathways involve atomic motions of different symmetries.$^{[101]}$ In chemical terms, this means that shortly past the TS, the molecule can be stabilized by breaking the local symmetry. Closer inspection of the reaction path by following the intrinsic reaction coordinates (IRC) should clarify the plausibility of linked reaction cycles.

Focusing on the TM cycle, substrate 2 coordinates to the intermediate $\lambda^3$-
4.2 ELECTROPHILIC TRIFLUOROMETHYLATION

Scheme 4.9: The late reductive elimination step of the transition metal-like catalytic cycle is induced by the concerted deprotonation of the coordinating substrate.

iodane 4 in a subsequent step to the insertion reaction. The final product 3 is then formed by another RE reaction (Scheme 4.9). Proceeding on the TM cycle is only possible, if benzotriazole 2 is favored over acetonitrile the coordination on 4. This is the case, assuming a simultaneous deprotonation of the coordinated 2 (Scheme 4.9), reducing its activation energy of the RE reaction to 3.3 kcal/mol. For both cycles, the first step is rate determining. But only in the TM cycle takes a similar role of a catalytic mediator (at least in the first step of the reaction cascade).

Further investigations showed that the initial barrier for the intra-molecular attack (valid for both cycles) is interfered by a competitive SN2 reaction. However, it appears that significant entropic contributions have a major impact on this rate determining step, which calls for a statistical mechanics approach. Due to this substantial solvent effect, the RE reaction is clearly favored over SN2 in the condensed phase. Note that reactions mediated by the Togni reagents can also release products of radical based processes (e.g. for S-nucleophiles). The exploration of such open shell routes is not part of this thesis, but specific projects are in preparation.
4.3 CONCLUSIONS

This final chapter was dedicated to chemically relevant reactions and the computational investigations were directed towards establishing a connection between insight of structure and bonding and the observed reactivity. Of particular importance are $\lambda^3$-iodane intermediates, formed \textit{in situ} in the reaction of diaryliodonium salts with nucleophiles. The present studies highlight the role of these iodanes, which act as “gateway” directing the reaction either towards reductive elimination reaction or towards a radical process, leading to a variety of products.

As reactive intermediates, $\lambda^3$-iodane species undergo rapid isomerization to a preferred configuration for the subsequent RE step. This is considered a Curtin-Hammett type reaction profile, which can be related to the polarity of the 3c-4e bond and the selectivity of the reductive elimination. However, structural constraints will take effect on the basic course of the reaction. If the aryl ligands bound to the iodine center are bridged, the strain on the hypervalent region will have an essential impact on the electronic landscape. Whereas for unstrained systems functionalization will be favored, we observe arene coupling and radical mechanisms for moderately or strongly strained systems. In the case of very strained systems, the reaction is forced towards a homolytic decomposition, as this is the only mechanism which is not influenced by strain of the hypervalent region (see Section 4.4).

For the subject of electrophilic trifluoromethylation by the Togni reagents, the DAFH analysis provided valuable insight into the activation process: protonation of DMTB results in a almost complete decoupling of the 3-center broken valence pairs. Even though the 3c-4e bond is essentially weaker, the reagent is still conformationally fixed and cannot perform isomerization. This results in a uniquely defined way to reductively eliminate an incoming nucleophile. With this reminiscence to transition metal chemistry, the exploration of the Ritter-type reaction opened up an alternative route, which branches into another possible reaction cycle.
4.4 FIRST PROSPECTS TOWARDS A DISSOCIATIVE ELECTRON TRANSFER

The presented studies were limited to the discussion of closed shell and singlet reactivity of $\lambda^3$-iodanes, in which we can resolve the observed reaction patterns in much simpler terms. At low temperatures, however, strained systems expose a distinctly different reactivity and only products of radical processes are found experimentally. A competitive radical reaction pathway could be the result of a single electron transfer (SET) mechanism. Another possibility, based on $\lambda^3$-iodane intermediate species, is the homolytic cleavage of the nucleophile-iodine bond (see Scheme 4.10). In both cases, a cyclic diaryliodine radical is the resulting intermediate.

Scheme 4.10: The homolytic cleavage of the 3-center bond is resulting in a diaryliodine and a nucleophile radical.

\[
\text{Scheme 4.10: The homolytic cleavage of the 3-center bond is resulting in a diaryliodine and a nucleophile radical.}
\]

The cleavage of the 3-center bond can be induced by thermal population of the lowest excited states, i.e. an internal dissociative electron transfer (DET) (see Figure 4.15). In order to achieve initial clarification of a possible DET mechanism, computations of the excited states of the bridged and unbridged diaryliodanes were already performed. These calculations reveal that the main contribution to the lowest excited state corresponds to a triplet excitation from the 3-center non-bonding to the 2-center antibonding orbital. The corresponding excitation energies can be thermally populated and fall within a narrow margin (e.g. $2.46 \pm 0.09 \text{ eV}$ for the azodiaryliodane series). The main component of this excitation is a $3\text{cb}^\text{nb} \rightarrow 2\text{cb}^*$ transition, which leads to an elongation of the 2-center bond, but not to its homolytic cleavage. The bond that breaks in the end is the 3-center bond, releasing an azo radical (see Figure 4.15). This is similar to the 3-center bond breaking process illustrated in Figure 4.9. The diaryliodine radical, which “captured” its electron from the $3\text{cb}^\text{nb}$, will be metastable.\cite{103}
From the perspective of the diaryliodonoium salt chemistry, the DET presents actually a side mechanism. The application of the Togni reagents, on the other hand, profits from radical processes in the event of favorable conditions. Further investigations for the exploration of radical reaction pathways by the means of *ab initio* molecular dynamics (AIMD) are in preparation. However, due to surface-hopping, final clarification is only possible by explicitly considering inter-system crossing along the DET reaction pathway.

![Figure 4.15: Evolution of the 3cb and 2cb* LNMOs of azo 1,1'-biphenyl iodane in the course of the thermal induced homolytic decomposition. The optimization of the first excited state results in a distinct elongation of the 3-center bond accompanied by a complete polarization of 3cb towards the azo ligand.](image)

4.5
Table 4.6: The natural charges of the ligand ipso-atoms $\delta_{\text{ipso}}$ in the syn- and anti-isomers of an array of diaryliodonanes (with $X = N_3, Br$). One of the two aryl ligands is a phenyl group present in all compounds and the other ligand is referred to as directing group. The partial charges highlighted correspond to the aryl ipso-atoms involved in the 3-center-4-electron bond (see figure below the table). Negative values for their difference $\Delta\delta_{\text{ipso}}$ indicate a dominating directing group.

<table>
<thead>
<tr>
<th></th>
<th>$X = N_3$</th>
<th></th>
<th>$X = Br$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{\text{ipso}}$(aryl)</td>
<td>$C_{\text{ipso}}$(phenyl)</td>
<td>$\Delta\delta_{\text{ipso}}$</td>
<td>$C_{\text{ipso}}$(aryl)</td>
</tr>
<tr>
<td>4-(OCH$_3$)Ph</td>
<td>anti</td>
<td>-0.35</td>
<td>-0.19</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.23</td>
<td>-0.31</td>
<td>-0.08</td>
</tr>
<tr>
<td>4-(NH$_2$)Ph</td>
<td>anti</td>
<td>-0.36</td>
<td>-0.19</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.24</td>
<td>-0.32</td>
<td>-0.08</td>
</tr>
<tr>
<td>o-tol</td>
<td>anti</td>
<td>-0.29</td>
<td>-0.20</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.20</td>
<td>-0.29</td>
<td>0.00</td>
</tr>
<tr>
<td>m-tol</td>
<td>anti</td>
<td>-0.30</td>
<td>-0.19</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.19</td>
<td>-0.30</td>
<td>0.00</td>
</tr>
<tr>
<td>p-tol</td>
<td>anti</td>
<td>-0.32</td>
<td>-0.19</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.20</td>
<td>-0.31</td>
<td>-0.01</td>
</tr>
<tr>
<td>4-(CF$_3$)Ph</td>
<td>anti</td>
<td>-0.29</td>
<td>-0.20</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.18</td>
<td>-0.32</td>
<td>0.14</td>
</tr>
<tr>
<td>4-(C$_3$H$_5$)Ph</td>
<td>anti</td>
<td>-0.33</td>
<td>-0.19</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.21</td>
<td>-0.31</td>
<td>-0.02</td>
</tr>
<tr>
<td>mesyl</td>
<td>anti</td>
<td>-0.30</td>
<td>-0.19</td>
<td>-0.02</td>
</tr>
<tr>
<td></td>
<td>syn</td>
<td>-0.20</td>
<td>-0.28</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

$^1$ 4-cyclopropyl phenyl
General Conclusions & Outlook

Give us insight, not numbers

Charles Coulson

The present work highlights $\lambda^3$-iodane compounds as excellent subjects for the study of multicenter bonding. These compounds strongly express their molecular orbitals according to the 3-center-4-electron bond model. The analysis of Domain Averaged Fermi Holes confirms actually the view of the CMO model, but offers a more detailed picture: coupling and decoupling patterns appeared to be a powerful tool to relate the multicenter picture with the chemistry of the $\lambda^3$-iodanes.

Be aware that our discussion of hypervalent bonding is restricted to compounds containing a central atom with a low coordination number. Compounds like $\lambda^3$-iodanes have the ability to reorganize their electronic structure by directing hybridization of iodine bond orbitals. This is due to the occurrence of “stereochemically active lone pairs”.\[5\] As a consequence, distinctive types of bonds are formed around the central atom, such as the 3c-4e bond*. This enables $\lambda^3$-iodanes to isomerize and react along unusual reaction patterns, in stark contrast to other hypervalent molecules, which are not affected by the PJT effect (see Figure 5.1).

The reason for the susceptibility of the electronic configuration of the CMOs of $\lambda^3$-iodanes to a pseudo Jahn-Teller (PJT) effect, is based on the molecular

*note that in absence of such active lone pairs, the s-orbital gets increasingly involved in all hypervalent bonds by symmetry
5 GENERAL CONCLUSIONS & OUTLOOK

symmetry. The T-shape geometry of $\lambda^3$-iodanes implies, in fact, the sharing of a p-orbital for the ligands arranged in trans position, giving rise to the 3c-4e bond picture. In particular, the hybridization of the iodine bond orbitals determines, whether the formation of new covalence is accompanied by an effective PJT stabilization or not.

The present thesis emphasizes, however, also the limit of the 3c-4e bond model. A quantum relativistic perspective of the iodine contact density reveals significant contraction of the valence s-shell with the consequence of hybridization defects. This observation awakes interest for further investigations of bonding patterns by the means of relativistic DAFH analysis. The same is true for exploring the impact of electron correlation to hypervalent bonding and the potential role of d-backbonding. In the end, it is the specific combination of ligands, which determines if multicenter bonding is a valid description for $\lambda^3$-iodanes or not.

Finally, breaking down the (closed shell) reactivity of $\lambda^3$-iodanes has confirmed that the hypervalent moiety is responsible for the versatile chemistry of iodanes. Quantum chemical calculations revealed the key role of $\lambda^3$-iodane intermediates being a "gateway" for all subsequent reactions. At the same time, the retention of planarity of the hypervalent region, again connected to a PJT effect, is beneficial in view of low reaction barriers for all reaction mechanisms. Given the revised Ritter-type reaction mechanism, it is of peculiar interest to explore, how the reagent can be directed towards running a transition metal-like reaction cycle.† As a final remark to the mechanistic considerations, it should be noted that all reactions are also prone to radical mechanisms, i.e. single or dissociative electron transfer (SET & DET).

Bridging the gap between quantum chemical information and the qualitative understanding of molecular structures and reactivities is the predominant purpose of most conceptual models. Accordingly, the present thesis emphasized important aspects of the chemistry of $\lambda^3$-iodanes and disclosed the ambivalent role of the 3c-4e bond model. In this light, the conclusions are not restricted to the class of $\lambda^3$-iodane compounds but do also account for a more general view of hypervalent bonding (Figure 5.1).

†nitrile insertion of transition metals lends itself for direct comparison[108–111]
Figure 5.1: Flow chart for determining the chemistry of hypervalent compounds (orange), in particular, \(\lambda^3\)-iodanes (blue). The requirement for the occurrence of a PJT effect is \(N_{1p} > 0\).
Appendix

A.1 THEORETICAL NOTES ON THE DAFH CODE

A.1.1 DERIVATION OF THE G-MATRIX FOR HF/KS-DFT IN AO BASIS

The exchange correlation density can be expressed in terms of a two-particle hole matrix

\[ h^{xc}(r_1, r_2; r'_1, r'_2) = \rho(r_1, r'_1) \rho(r_2, r'_2) - \rho(2)(r_1, r_2; r'_1, r'_2), \quad (A.1) \]

containing the pair density matrix \( \rho^{(2)} \). For a single determinant and closed shell system the pair the density fulfills

\[ \rho^{(2)}(r_1, r_2; r'_1, r'_2) = \left| \begin{array}{cc} \rho(r_1, r'_1) & \rho(r_2, r'_1) \\ \rho(r_1, r'_2) & \rho(r_2, r'_2) \end{array} \right|, \quad (A.2) \]

which simplifies eq. (A.1):

\[
\begin{align*}
    h^{xc}(r_1, r_2; r'_1, r'_2) &= \rho(r_1, r'_1) \rho(r_2, r'_2) - \rho(r_1, r'_1) \rho(r_2, r'_2) - \rho(r_1, r'_2) \rho(r_2, r'_1) \\
    &= \rho(r_1, r'_2) \rho(r_2, r'_1) \\
    &= \sum_{ij}^{\text{occ}} \phi_i(r_1) \phi_i^*(r_2) \phi_j(r_2) \phi_j^*(r'_1),\quad (A.3)
\end{align*}
\]

Integration of the exchange correlation density \( h^{xc} \) against the coordinate \( r_2 \) over an atomic domain \( A \), in this code corresponding to an atom basin of the quantum theory of atoms in molecules (QTAIM), results in the formulation of
the domain averaged Fermi hole $g_A$

$$g_A(r_1, r'_1) = \int w_A(r_2) \rho^{xc}(r_1, r_2; r'_1, r'_2) \delta(r_2 - r'_2) \, dr_2 \, dr'_2$$

$$= \sum_{ij}^{occ} \phi_i(r_1) \left[ \int w_A(r_2) \phi_i^*(r_2) \phi_j(r'_2) \delta(r_2 - r'_2) \, dr_2 \, dr'_2 \phi_j^*(r'_1) \right]$$

$$= \sum_{ij}^{occ} \phi_i(r_1) S_{ij}^A \phi_j^*(r'_1) = \sum_{ij}^{occ} \phi_i(r_1) G_{ij}^A \phi_j^*(r'_1) , \quad (A.5)$$

containing the atomic overlap matrix (AOM) in an atomic orbital basis. For chemical interpretation it is useful to transform the inter orbital product $\phi_i(r_1)\phi_j^*(r_1)$ to an intra orbital product $\phi_k(r_1)\phi_j^*(r_1)$ by using the diagonal of the G-matrix $\tilde{G}^A = XG^AX^\dagger$:

$$g_A(r_1) = \sum_{ij}^{occ} \phi_i(r_1) G_{ij}^A \phi_j^*(r_1)$$

$$= \sum_{ijklmn} \phi_i(r_1) X_{ik}^\dagger X_{kl} G^A_{ln} X_{nm} X_{mj} \phi_j^*(r_1)$$

$$= \sum_{ijklm} \phi_i(r_1) X_{ik}^\dagger \tilde{G}_{km} A_{lm} X_{mj} \phi_j^*(r_1)$$

$$= \sum_{ijkl} \phi_i(r_1) X_{ik}^\dagger \tilde{G}^A_{kl} X_{kj} \phi_j^*(r_1)$$

$$= \sum_k \sum_i X_{ki}^\dagger \phi_i(r_1) \tilde{G}^A_{kk} \sum_j X_{kj} \phi_j^*(r_1) \quad (A.6)$$

The eigenvectors X of $G^A$ transform the AOs into a set of nonorthogonal 1-particle functions $\psi_k = \sum_i X_{ki}^\dagger \phi_i(r_1)$ resulting finally

$$\Rightarrow g_A(r_1) = \sum_k^{occ} \psi_k(r_1) \tilde{G}^A_{kk} \psi_k^*(r_1) . \quad (A.7)$$
A.1 THEORETICAL NOTES ON THE DAFH CODE

To extend the AIM domain $\Omega$ over more than a single atom, the QTAIM weight functions $w_\Omega(r)$ can be summed up:

$$g_\Omega(r_1, r'_1) = \int w_\Omega(r_2) \rho^{xc}(r_1, r_2; r'_1, r'_2) \delta(r_2 - r'_2) \, dr_2 \, dr'_2$$

$$= \int [w_A(r_2) + w_B(r_2)] \rho^{xc}(r_1, r_2; r'_1, r'_2) \delta(r_2 - r'_2) \, dr_2 \, dr'_2$$

$$= \sum_{ij}^{occ} \phi_i(r_1) \left[ \int w_A(r_2) \phi_i^*(r_2) \phi_j(r'_2) \delta(r_2 - r'_2) \, dr_2 \, dr'_2 \right. + \left. \int w_B(r_2) \phi_i^*(r_2) \phi_j(r'_2) \delta(r_2 - r'_2) \, dr_2 \, dr'_2 \right] \phi_j^*(r'_1)$$

$$= \sum_{ij}^{occ} \phi_i(r_1) \left[ S^A_{ij} + S^B_{ij} \right] \phi_j^*(r'_1)$$

$$= \sum_{ij}^{occ} \phi_i(r_1) G_\Omega^{ij} \phi_j^*(r'_1), \quad (A.8)$$

A.1.2 Isopycnic Transformation of the G-Matrix

Knowledge of the one-particle density matrix (1-RDM) $\rho(r, r')$ is sufficient to calculate the total energy. The isopycnic transformation is a generalization of orbital transformations to natural spin-orbitals.\cite{22} It guarantees the invariance of the 1-RDM and orthonormality of the natural spin-orbitals

$$\rho(r, r') = \sum_i \eta_i \psi_i(r) \psi_i^*(r'), \quad \langle \psi_i | \psi_i \rangle = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}, \quad (A.9)$$

and therefore any linear transformation $\varphi_i(r) = \sum_j T_{ij}^f \psi_j(r)$ lets the 1-RDM unchanged. We adopt this procedure for our G matrix, which has an equivalent structure with the eigenvalues of the AOM as occupation numbers $\tilde{G}_\Omega^{A \eta_i} = \eta_i$:

$$g_A(r) = \sum_i \eta_i \psi_i(r) \psi_i^*(r). \quad (A.10)$$
The isopycnic condition for the 1-RDM or the G matrix, respectively,

\[
g_A(r) = \sum_i \eta_i \psi_i(r) \psi_i^*(r) = \sum_j \nu_j \varphi_j(r) \varphi_j^*(r) \tag{A.11}
\]

allows us to express the transformation matrix by the occupation numbers and a rotation matrix

\[
\eta_{kl} = \sqrt{\eta_k} \sqrt{\eta_l} = \sum_j T_{kj}^\dagger \nu_j T_{jl} = \sum_j T_{kj}^\dagger \sqrt{\nu_j} \sqrt{\nu_j} T_{jl} \tag{A.12}
\]

\[
\to \eta_{k1} \psi_k(r) \psi_1^*(r) = \sum_{kl} \eta_k \delta_{kl} \psi_k(r) \psi_l^*(r)
\]

\[
= \sum_k \eta_k \psi_k(r) \sum_l \delta_{kl} \psi_l^*(r) = \sum_k \eta_k \psi_k(r) \psi_k^*(r)
\]

\[
\to g_{k1}^A = g_{jj}^A = g_{kk}^A,
\]

In addition, the transformed occupation numbers \(\nu_j\) are defined by normalization condition.

\[
\int \psi_i(r) \psi_i^*(r) \, dr = \sum_{kl} \int T_{jk} \varphi_k(r) T_{jl}^\dagger \varphi_l^*(r) \, dr = \sum_{kl} T_{jk} T_{jl}^* S_{kl} \tag{A.13}
\]

\[
= \sum_{kl} T_{jk} T_{jl}^* \int \varphi_k(r) \varphi_l^*(r) \, dr = \sum_{kl} T_{jk} T_{jl}^* S_{kl}
\]

\[
= \sum_k T_{jk} T_{jk}^* S_{kk} = \sum_k \sqrt{\eta_k} \sqrt{\eta_k} U_{jk} \sqrt{\nu_j} \sqrt{\nu_j} U_{jk}^* S_{kk}
\]

\[
\to \nu_j = \sum_k \eta_k U_{jk} U_{jk}^* S_{kk} \tag{A.14}
\]
A.1.3 Localization Scheme

It was shown that the isopycnic transformation is composed of the occupation numbers and unitary transformations $U_{k_1}$. These transformations are found in a localization procedure based on the localization index sum\cite{22}

$$L = \sum_i L_i = \sum_{\Lambda} \sum_i \langle i | i \rangle_{\Lambda}^2,$$  \hspace{1cm} (A.15)

containing the localization index $L_i$ of the $i$th spin-orbital, but it has to be adapted to our purpose of localizing the G matrix. Hence, the AOMs are first transformed with the eigenvectors $X^\Lambda$ of the basin specific AOM:

$$\langle i | j \rangle_{\Lambda} = \int w_{\Lambda}(r) \phi_i(r) \phi_j^*(r) \, dr \hspace{1cm} (A.16)$$

$$\rightarrow \langle a | b \rangle_{\Lambda} = \int w_{\Lambda}(r) \psi_a(r) \phi_j^*(r) \, dr$$

$$= \int w_{\Lambda}(r) \sum_i \phi_i(r) (X^\Lambda)^{\dagger}_{ia} \sum_j (X^\Lambda)^{\dagger}_{bj} \phi_j^*(r) \, dr$$

$$= \sum_{ij} \int w_{\Lambda}(r) \phi_i(r) (X^\Lambda)^{\dagger}_{ia} \phi_j^*(r) X^\Lambda_{bj} \, dr$$

$$= \sum_{ij} \int w_{\Lambda}(r) \phi_i(r) \phi_j^*(r) \, dr (X^\Lambda)^{\dagger}_{ia} X^\Lambda_{jb}$$

$$= \sum_{ij} \langle i | j \rangle_{\Lambda} (X^\Lambda)^{\dagger}_{ia} X^\Lambda_{jb} \hspace{1cm} (A.17)$$

79
The generalized localization index includes the values $\nu_a$ of the basin specific AOM and the adapted localization scheme now maximizes

$$L = \sum_a \nu_a^2 L_a = \sum_a \nu_a^2 \sum_\Lambda \langle a | a \rangle_\Lambda^2 \quad (A.18)$$

$$= \sum_\Lambda \sum_a \nu_a^2 \left( \sum_{kl} T_{ak}^* T_{al} \langle k | l \rangle_\Lambda \right)^2$$

$$= \sum_\Lambda \sum_a \nu_a^2 \left( \sum_{kl} \sqrt{\eta_k} U_{ak}^* \sqrt{\eta_l} U_{al} \langle k | l \rangle_\Lambda \right)^2$$

$$= \sum_\Lambda \sum_a \left( \sum_{kl} \sqrt{\eta_k \eta_l} U_{ak}^* U_{al} \langle k | l \rangle_\Lambda \right)^2 \quad \times (A.19)$$


### A.1.4 Localization Procedure

**Optimal Angle**

The unitary transformation of eq. (A.19) are computed through a series of $2 \times 2$ Jacobi rotations

$$L = \sum_\Lambda \left( \cos^2 \alpha \sqrt{\eta_k \eta_k} \langle k | k \rangle_\Lambda + 2 \sin \alpha \cos \alpha \sqrt{\eta_k \eta_l} \langle k | l \rangle_\Lambda + \sin^2 \alpha \sqrt{\eta_l \eta_l} \langle l | l \rangle_\Lambda \right)^2$$

$$+ \left( \sin^2 \alpha \sqrt{\eta_k \eta_k} \langle k | k \rangle_\Lambda - 2 \sin \alpha \cos \alpha \sqrt{\eta_k \eta_l} \langle k | l \rangle_\Lambda + \cos^2 \alpha \sqrt{\eta_l \eta_l} \langle l | l \rangle_\Lambda \right)^2 \quad \times (A.20)$$

Therefore, we need to find the optimal angle $\alpha$ for each rotation to maximize the localization sum:

$$\frac{\partial}{\partial \alpha} L = -\sin(4\alpha) \left[ (\sqrt{\eta_k \eta_k} \langle k | k \rangle_\Lambda - \sqrt{\eta_l \eta_l} \langle l | l \rangle_\Lambda)^2 - 4 \sqrt{\eta_k \eta_l} \langle k | l \rangle_\Lambda^2 \right]$$

$$+ 4 \cos(4\alpha) \sqrt{\eta_k \eta_l} \langle k | l \rangle_\Lambda \left[ \sqrt{\eta_k \eta_k} \langle k | k \rangle_\Lambda - \sqrt{\eta_l \eta_l} \langle l | l \rangle_\Lambda \right]$$

$$= 0 \quad (A.21)$$
A.1 THEORETICAL NOTES ON THE DAFH CODE

$$\Rightarrow \alpha = \frac{1}{4} \arctan \left( \frac{4 \sqrt{\eta_{k} \eta_{l}} \langle k | l \rangle_{A} \left[ \sqrt{\eta_{k} \eta_{k}} \langle k | k \rangle_{A} - \sqrt{\eta_{l} \eta_{l}} \langle l | l \rangle_{A} \right]}{\left( \sqrt{\eta_{k} \eta_{k}} \langle k | k \rangle_{A} - \sqrt{\eta_{l} \eta_{l}} \langle l | l \rangle_{A} \right)^{2} - 4 \sqrt{\eta_{k} \eta_{l}} \langle k | l \rangle_{A}^{2}} \right)$$

(A.22)

Eq. (A.20) is rearranged rigorously before attaining to the derivative eq. (A.21).

In the code, a shorthand notation is introduced $\sqrt{\eta_{k} \eta_{l}} \langle k | l \rangle_{A} = \langle \tilde{k} | \tilde{l} \rangle_{A}$ to compute $\alpha$.

Transformations

This angle is used now for the rotation matrix and allows to transform the occupation numbers with eq. (A.14) iteratively (specific written out for a $2 \times 2$ rotation, which involves two occupation number vectors at a time)

$$v_{i} = \sum_{k} \eta_{k} U_{ik}^{*} U_{ik} S_{ik} = \sum_{k} \eta_{k} U_{ik}^{*} U_{ik} \sum_{A} S_{ik}^{A} = \eta_{i} \cos^{2} \alpha \sum_{A} S_{ii}^{A} + \eta_{k} \sin^{2} \alpha \sum_{A} S_{kk}^{A} + 2 \sqrt{\eta_{i} \eta_{k}} \sin \alpha \cos \alpha \sum_{A} S_{ik}^{A}$$

$$v_{j} = \eta_{j} \sin^{2} \alpha \sum_{A} S_{jj}^{A} + \eta_{k} \cos^{2} \alpha \sum_{A} S_{kk}^{A} + 2 \sqrt{\eta_{j} \eta_{k}} \cos \alpha \sin \alpha \sum_{A} S_{jk}^{A}$$

and the AOMs

$$\langle i | j \rangle_{A} = \sum_{kl} T_{ik}^{*} T_{jl} \langle k | l \rangle_{A}$$

$$= \sum_{kl} \sqrt{\eta_{k} \eta_{l}} U_{ik}^{*} U_{jl} \langle k | l \rangle_{A} .$$

Specific for the $2 \times 2$ transformation block:

$$\langle i | j \rangle_{A} = \sqrt{\frac{\eta_{k} \eta_{k}}{v_{i} v_{i}}} (- \sin \alpha \cos \alpha) \langle k | k \rangle_{A}$$

$$+ \sqrt{\frac{\eta_{k} \eta_{l}}{v_{i} v_{j}}} (\cos^{2} \alpha) \langle k | l \rangle_{A}$$

$$+ \sqrt{\frac{\eta_{l} \eta_{k}}{v_{j} v_{i}}} (- \sin^{2} \alpha) \langle l | k \rangle_{A}$$

$$+ \sqrt{\frac{\eta_{l} \eta_{l}}{v_{j} v_{j}}} (\sin \alpha \cos \alpha) \langle l | l \rangle_{A}$$

(A.24)
and the off-block elements:

\[
\langle i | k \rangle_A = \sum_l T^*_{il} \langle l | k \rangle_A = \sum_l \sqrt{\frac{\eta_l}{\nu_i}} U^*_{il} \langle l | k \rangle_A \tag{A.25}
\]

\[
= \sqrt{\frac{\eta_i}{\nu_i}} \cos \alpha \langle i | k \rangle_A + \sqrt{\frac{\eta_j}{\nu_i}} \sin \alpha \langle j | k \rangle_A
\]

\[
\langle j | k \rangle_A = \sqrt{\frac{\eta_i}{\nu_j}}(-\sin \alpha)\langle i | k \rangle_A + \sqrt{\frac{\eta_j}{\nu_j}} \cos \alpha \langle j | k \rangle_A
\]

### A.1.5 Transformation of the MO Coefficients

First, the MO coefficients have to be transformed with the eigenvectors \(X^A\) of the specific AOM

\[
\psi_k = \sum_i (X^A)^\dagger_{ki} \phi_i(r_1) \quad \simeq \sum_i X^A_{ik} \phi_i(r_1). \tag{A.26}
\]

This new set of orbitals or the coefficient matrix, respectively, is subsequently transformed using the transformation matrix of the isopycnic transformation (eq. (A.13))

\[
\varphi_b = \sum_a C^\dagger_{ba} \psi_a
\]

\[
\tilde{C}_{ak} = \sum_j T^\dagger_{kj} C_{aj} = \sum_j T_{jk} C_{aj} = \sum_j \sqrt{\frac{\eta_k}{\nu_j}} U_{jk} C_{aj} \tag{A.27}
\]
Appendix

B.1 THE DAFH CODE

******************************************************************************
!* ANALYSIS OF DOMAIN AVERAGED FERMI HOLES
!* Program written by Halua Pinto de Magalhaes
!* Parts of the isopycnic transformation were written
!* by Patrick Bultinck from the Ghent quantum chemistry group
!*-----------------------------------------------------------------------------
!* This is a small program to perform domain averaged fermi hole
!* analysis on a level of closed shell single determinant theory.
!* The procedure contains a isopycnic transformation
!* with 2x2 Jacobi rotations to result in a new set of naturals
!* that are constrained to remain orthonormal. At present this is
!* only possible for Hartree-Fock as the naturals are strictly
!* degenerate eigenfunctions of the density matrix as an operator.
!* The input is the Atomic Overlap Matrix (AOM) generated by AIMAll
!* program suite and the formatted checkpoint file from a Gaussian 09
!* calculation.
!*-----------------------------------------------------------------------------
!* In order to use it, please supply two input files and the AIM basin region
!* (atom numbers) as shown with the following command:
!*-----------------------------------------------------------------------------
!* ./dafh.x -A'atom1' [-B'atom2' -C'atom3' ...] 'wfx-file'.wfx 'fromcheck-file'.fchk
!*-----------------------------------------------------------------------------
!* where the atom numbers of the integrated AIM basin region are first defined
!* with "-X'atom#'" [or "-all", see bellow] (the order of atom numbers is irrelevant),
!* followed by the input files (the order of the arguments is irrelevant).
******************************************************************************
B APPENDIX

!* Possible additional options:
!* ./dafh.x [...] -noiso -print -all
!* for analysis without isopycnic transformation and/or printing AOMs.
!* (printing is only default for small molecules with small basis sets).
!* "-all" defines the entire molecule as basin (results in localized orbitals).
!* -all defines the entire molecule as basin (results in localized orbitals).
!* IMPORTANT:
!* - Run the program by keeping the same subdirectory structure as
!* generated by the AIMALL integration: the atomic files are in a
!* subdirectory named 'AIMALL-calc-name'_atomicfiles.
!* - Compilation: Provide the links to libraries (BLAS and LAPACK)
!* used by the dsyev routine (inside of the diagonalization subroutine
!* in this code) along with your fortran compiler.
!*-------------------------------------------------------------
!* IMPORTANT:
!* - Run the program by keeping the same subdirectory structure as
!* generated by the AIMALL integration: the atomic files are in a
!* subdirectory named 'AIMALL-calc-name'_atomicfiles.
!* - Compilation: Provide the links to libraries (BLAS and LAPACK)
!* used by the dsyev routine (inside of the diagonalization subroutine
!* in this code) along with your fortran compiler.
!*-------------------------------------------------------------
!* Program based on the following article:
!* Partitioning of the orbital overlap matrix and the localization criteria
!* ****************************************************************************

module dafh_data
  implicit none

  INTEGER,DIMENSION(1000)::basin !aim basin region (atom numbers)
  REAL*8,DIMENSION(:),ALLOCATABLE::occ !eigenvalues of chosen AOM ==
      occupation numbers
  REAL*8,DIMENSION(:),ALLOCATABLE::newocc !auxiliary
      transformed occ numbers
  REAL*8,DIMENSION(:),ALLOCATABLE::occ_noiso !auxiliary for non-isop.
      transformed occ numbers
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::totmat !matrix of total AOM sum
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::eigenval !eigenvalues of sorted AOM
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::diagmat !eigenvalues of AOMs
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::coeff !MO coefficient matrix
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::c2 !auxiliary MO coefficient matrix
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::trf !MO coefficient transformation
      matrix
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::aimsmat !AOMs sorted by the specific atoms
      as from AIMAll output
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::taimsmat !transpose of sorted AOMs
  REAL*8,DIMENSION(:,,:),ALLOCATABLE::nevmat !auxiliary AOM for rotation
      procedure
B.1 THE DAFH CODE

```fortran
CHARACTER(90)::inputfile,outputfile !input file names and parameters
CHARACTER(90)::wfxfile,wfxname,fchkfile,fchkname
CHARACTER(10)::atomnr
CHARACTER(30)::label_lower,label_upper
INTEGER::num_orb,num_occ,num_atoms !number of orbitals, atoms, basis fct.
INTEGER::num-bsf,num-bsftot,bsn,core
REAL*8::L_index !localization index
LOGICAL::isoflag,printflag,molflag,lindepflag

end module dafh_data

!*****************************************************************************
!*CONTROL CENTRE
!******************************************************************************
program dafh
USE dafh_data
implicit none
INTEGER::a,x,y,z,arg
CHARACTER(150)::iarg,cmd,tempfile
CHARACTER(30)::tmp,inp
REAL::r

!1. get input file names and parameters
arg = iargc()
isoflag = .true.
printflag = .false.
molflag = .false.
lindepflag = .false.
bsn = 0
basin = 0

do a=1, arg
call getarg(a,inputfile)
x = len(trim(inputfile)) - 4
y = len(trim(inputfile)) - 5
z = len(trim(inputfile))
if(inputfile((x+1):z).eq.".wfx") then
  wfxfile = trim(inputfile)
wfname = inputfile(1:x)
elseif(inputfile((y+1):z).eq.".fchk") then
  fchkfile = trim(inputfile)
fchkname = inputfile(1:y)
elseif(trim(inputfile).eq."-noiso") then
  isoflag = .false.
elseif(trim(inputfile).eq."-print") then
```

85
printflag = .true.

elseif(trim(inputfile).eq."-all") then
  molflag = .true.
  inp = "all"
else
  read(inputfile(3:),'(I3)') basin(a)
  bsn = bsn + 1
  inp = inputfile(3:)
endif
enddo

! write output temporary file
  call init_random_seed()
  call RANDOM_NUMBER(r)
  write(tmp,'(F8.4)') r
  if(isoflag) then
    write(tempfile,'(A)') trim(wfxname)//"_noiso"//trim(inp)//".temp_dafh"//trim(adjustl(tmp))
  else
    write(tempfile,'(A)') trim(wfxname)//"_"//trim(inp)//".temp_dafh"//trim(adjustl(tmp))
  endif
  open(16,File=tempfile,ACCESS='sequential',STATUS='new')
  write(16,*)

!2. read in atomic overlap matrices and formatted checkpoint file
  call read_aom
  call read_fchk

!3. diagonalize ADMs
  call diagonalize

!4. isopycnic transformation of ADMs
  call isopycnic

!5. write formatted checkpoint file
  call write_fchk

!6. write output file
  close(16)
  write(outputfile,'(A90)') trim(fchkname)//"_dafh_"//trim(label_lower)//".out"
B.1 THE DAFH CODE

```fortran
B.1.1 THE DAFH CODE

```cmd = "mv //trim(tempfile)";//".//adjustl(trim(outputfile))
call SYSTEM(cmd)
end program dafh

!**************************************************************************
!READ IN AOMs
!**************************************************************************
subroutine read_aom

USE dafh_data
implicit none

INTEGER::a,b,atom,num_el
INTEGER::i,j,k,l

CHARACTER(90)::line1,line2
CHARACTER(90)::intpath,title,tmp,capitalize
CHARACTER(10)::lower,decapitalize
LOGICAL::ecpflag = .false.

!construct path of subdirectory
intpath = trim(wfxname) // "atomicfiles/"

!open wfx file to get molecular informations to allocate matrices
open(13,file=trim(wfxfile),status="old",access="sequential")
do
read(13,'(A90)') line1
if (line1(1:7).eq."<Title>" then
  read(13,'(A90)') title
  core = 0
  if (title(1:8).eq."ECP-MO:" then
    read(title(9:13),'(I5)') core
    ecpflag = .true.
  endif
  endif
elseif (line1(1:18).eq."<Number of Nuclei>" then
  read(13,*) num_atoms
elseif (line1(1:13).eq."<Number of El>" then
  read(13,*) num_el
  num_el = num_el - core
  num_occ = num_el/2
  num_orb = num_occ
elseif (line1(1:16).eq."<Number of Alpha>" then
  read(13,*) num_occ
  exit
endif
dendo
if(molflag) then
bsn = num_atoms
    do i=1, bsn
        basin(i) = i
    enddo
endif
write(tmp,'(I10)') num_orb
if(len(trim(adjustl(tmp))).gt.2) then
    a = len(trim(adjustl(tmp))) - 2
else
    a = 1
endif
write(16,'(31XA17)') adjustl(trim(capitalize(wfxfile)))
write(16,'(27XA)',advance="no") "=========================
    do i=1, a; write(16,'(A)',advance="no") "; endif
write(16,’*’)
write(16,’(28XA20,13)’) ”Number of atoms”,num_atoms
write(16,’(28XA20,13)’) ”Number of orbitals”,num_orb
write(16,’(27XA)’,advance="no") ”=========================
    do i=1, a; write(16,’(A)’,advance="no") "; endif
write(16,’*’)
if(ecpflag) write(16,’(28XA22)’) ”ECP-MO in AIM calc.”
! allocate arrays with read-in parameters
allocate(occ(num_orb))
allocate(newocc(num_orb))
allocate(occ_noiso(num_orb))
allocate(eigenval(num_atoms,num_orb))
allocate(totmat(num_orb,num_orb))
allocate(trf(num_orb,num_orb))
allocate(ttrans(num_orb,num_orb))
allocate(diagmat(num_orb,num_orb))
allocate(aimsmat(num_atoms,num_orb,num_orb))
allocate(taimsmat(num_atoms,num_orb,num_orb))
allocate(newmat(num_atoms,num_orb,num_orb))

occ=0.0
newocc=0.0
occ_noiso=0.0
eigenval=0.0
totmat=0.0
trf=0.0
ttrans=0.0
diagmat=0.0
aimsmat=0.0
taimsmat=0.0
newmat=0.0
label_lower=""
B.1 THE DAFH CODE

label_upper=""

! read in AOMs from atomic files in subdirectory
write(16,*)
write(16,*)
write(16,*) "Reading input files...
if(num_orb.lt.5) printflag = .true.
if(printflag) then
write(16,*)
write(16,*) "AOMs
---------------------------------------------------------------------------"
endif

do
read(13,'(A90)') line1
if (line1(1:15).eq."<Nuclear_Names>") then
  do atom=1, num_atoms
    read(13,'(A10)') atomnr
    lower = decapitalize(atomnr)
    do a=1, bsn
      if(atom.eq.basin(a)) then
        label_lower = trim(label_lower) // trim(lower(2:))
        label_upper = trim(label_upper) // trim(atomnr)
      endif
    enddo
    b = atom + 17 ! file number + 1 higher than static numbered files in entire code
    open(b,file=trim(intpath)//trim(lower(2:))//".int",status="old",access="sequential")
  enddo
  b = atom + 17 ! file number + 1 higher than static numbered files in entire code
  do i=1, num_orb
    do j=i, num_orb
      aimsmat(atom,i,j)=aimsmat(atom,j,i)
    enddo
  enddo
endif
enddo

open(b,file=trim(intpath)//trim(lower(2:))//".int",status="old",access="sequential")
  do
    read(b,'(A90)') line2
    if (line2(1:27).eq."The_Atomic_Overlap_Matrix:") then
      do i=1,3;read (b,*);enddo
      do i=1,num_orb
        read (b,'(6F14.10)') (aimsmat(atom,i,j),j=1,num_orb)
      enddo
    endif
    exit
  enddo
enddo

enddo

close(b)

do i=1, num_orb
  do j=1, num_orb
    aimsmat(atom,i,j)=aimsmat(atom,j,i)
  enddo
enddo

! print labeled AOM
if(printflag) then
  write(16,'(6XA5)') atomnr
  do i=1,num_orb
    write(16,'(1000F11.7)') (aimsmat(atom,i,j),j=1,num_orb)
B APPENDIX

!---------------------------------------------
!check if they sum up to a unit matrix
!---------------------------------------------
if(printflag) then
  write(16,*) "TOTAL SUM OF AOMs"
endif

do k=1,num_orb
  do l=1,num_orb
    totmat(k,l)=0.0
    do atom=1,num_atoms
      totmat(k,l)=totmat(k,l)+aimsmat(atom,k,l)
    enddo
  enddo
if(printflag) then
  write(16,'(1000F11.7)') (totmat(k,l),l=1,num_orb)
endif
enddo
end subroutine read_aom

!******************************************************************************
!*READ IN FORMATTED CHECKPOINT FILE
!*******************************************************************************
subroutine read_fchk
!read in MO coefficients which are transformed simultaniously with the AOMs
!later and used for visualization
USE dafh_data
implicit none

INTEGER::istat
CHARACTER(90)::line

!the number of basis functions is needed if linear dependencies occur
open (14,file=trim(fchkfile),status="old",access="sequential")
do
  read(14,'(A90)') line
  if (line(1:15).eq."Number of basis") then
    read (line,'(57X,I4)') num_bsftot
  elseif (line(1:13).eq."Number of ind") then
    read (line,'(57X,I4)') num_indtot
  end if
enddo
end subroutine read_fchk
B.1 THE DAFH CODE

read (line,’(57X,14)’) num_bsf
exit
endif
enddo

!if linear dependencies occur the coefficient matrix isn’t a square matrix
!but only linear independent basis functions will be transformed later
if (num_bsf/=num_bsftot) then
lindepflag = .true.
write(16,*)
write(16,*)
write(16,’(13XA)’) ”>>>ATTENTION: linear dependent functions cut-off<<<”
write(16,*)
write(16,*)
endif
allocate(coeff(num_bsftot,num_bsftot))
allocate(c2(num_bsftot,num_bsftot))
coeff=0.0
c2=0.0
do
read(14,’(A90)’) line
if(line(1:49).eq. ”Alpha MO coefficients R NN=”) then
read(14,’(5E16.8)’) ((coeff(i,j),i=1,num_bsftot),j=1,num_orb)
exit
endif
enddo
end subroutine read_fchk
B APPENDIX

lwork=100*num_orb
allocate(work(lwork))
work=0.0
temp_aom=0.0
trace=0.0

do a=1, bsn
do i=1, num_orb
do j=1, num_orb
   temp_aom(i,j)=aimsmat(basin(a),i,j)
eddo
eddo
diagmat=diagmat+temp_aom
eddo
do i=1, num_orb
   trace(i)=diagmat(i,i)
eddo
call dsyev('V','L',num_orb,diagmat,num_orb,occ,work,lwork,info)

if(printflag) then
   write(16,*)
   write(16,*)
endif
write(16,*) "* Diagonalizing AOMs of selected atoms..."
write(16,*)
if(molflag) then
   write(16,'(2XA9)') "BASIN ALL"
   write(16,'(X)') "=========="
else
   write(16,'(2XA5,A)') "BASIN", label_upper
   write(16,'(X)') "="
   do i=1, len(trim(label_upper)); write(16,'(A)',advance="no") =
   write(16,*)
endif
write(16,'(2XA,F16.8)')"> population of basin: N=", 2*sum(trace)
write(16,*)
write(16,*) "initial occ
---------------------------------------------------------------------"
write(16,'(5E16.8)') (2*occ(i),i=1,num_orb)
write(16,*)
if(printflag) then
   write(16,*)
   write(16,*) "eigenvectors
---------------------------------------------------------------------"
write(16,'(X,1000(I6,5X))')(i, i=1, num_occ)
do i=1, num_orb
   write(16,'(1000F11.7)') (diagmat(i,j),j=1,num_orb)
B.1 THE DAFH CODE

```fortran
    enddo
    endif
    if(isoflag) then
    else
        occ_noiso=occ
    endif
    ! check successful diagonalization: the sum of all occupation numbers
    ! should result in the total number of orbitals
    ! write(16,*)
    ! write(16,'(2XA',advance="no") "> Check total occ. sum:  
    ! temp_aom=0.0
    ! do atom=1, num_atoms
    ! do i=1, num_orb
    ! do j=1, num_orb
    ! temp_aom(i,j)=aimsmat(atom,i,j)
    ! enddo
    ! enddo
    ! do i=1, num_orb
    ! temp_trace(i)=temp_aom(i,i)
    ! enddo
    ! call dsyev('V','L',num_orb,temp_aom,num_orb,temp_occ,work,lwork,info)
    ! do i=1, num_orb
    ! eigenval(atom,i)=temp_occ(i)
    ! enddo
    ! tempsum(atom)=sum(temp_occ)
    ! write(16,'(F4.2,A)',advance="no") tempsum(atom), " + 
    ! enddo
    ! write(16,'(A,F10.2)') " = ", sum(tempsum)
    ! write(16,*) "-----------------------------------------------------------------------------"
    ! write(16,'(2XA,F16.8)') "trace of diagonalized G-matrix(sum of eigenvalues):" , 2*sum(occ)
    ! write(16,'(2XA,E16.8)') "precision:", abs(sum(trace)-sum(occ))
end subroutine diagonalize

!******************************************************************************

! isopycnic transformation
!******************************************************************************
subroutine isopycnic
    use dafh_data
    implicit none
    REAL*8,DIMENSION(:,:),ALLOCATABLE::tempmat
    REAL*8,DIMENSION(:,:),ALLOCATABLE::temptrans
    integer::i,j,k,l,n,o
```

93
515  integer::atom,startmo
516  integer::iter=0
517  integer::maxit=500
518
519  real*8::pi=3.1415926535897932384626433
520  real*8::bigratio=1.0e12
521  real*8::small=1.0e-18
522  real*8::conver=1.0e-6
523  real*8::alpha
524  real*8::nomin,dendenom
525  real*8::l_old
526  real*8::rotorii,rotorik,rotorki,rotorkk
527
528  allocate(tempmat(num_orb,num_orb))
529  allocate(temptrans(num_orb,num_orb))
530  tempmat=0.0
531  temptrans=0.0
532
533  ! comment call to subroutine if formatted checkpoint file not provided
534  call mo_transf(iter)
535
536  ! transform aoms with the eigenvectors of the basin specific aoms
537  do atom=1, num_atoms
538      tempmat=0.0
539      do i=1,num_orb
540         do j=1,num_orb
541            do k=1,num_orb
542               tempmat(i,j)=tempmat(i,j)+diagmat(k,i)*aimsmat(atom,k,j)
543            enddo
544            enddo
545         enddo
546      enddo
547      do i=1,num_orb
548         do j=1,num_orb
549            do l=1,num_orb
550               aimsmat(atom,i,j)=aimsmat(atom,i,j)+tempmat(i,l)*diagmat(l,j)
551            enddo
552         enddo
553      enddo
554      aimsmat=0.0
555      tempmat=0.0
556
557  ! Start computing the value of the
558  ! localization index L=sum_atoms[sum_orbitals[(<i|i>_A)**2]]
559  ! and we optimize the rotation angle that maximizes L in a
560  ! 2x2 rotation fashion. Please see theoretical notes where
561  ! needed.
562  startmo=1
563  do i=1,num_orb
564     if (occ(i).lt.1e-18) then
B.1 THE DAFH CODE

\begin{verbatim}
      startno=startno+1
      occ(i)=0.0D0
      endif
      enddo

! Call the subroutine that will compute the starting value of L
      call local(taimsmat,occ,num_atoms,num_orb,L_index)
      write(16,*)
      write(16,*)
      write(16,*) "* Starting localization index: L_index"
      write(16,*) "> Transforming AOMs and MO coefficients"
      write(16,*)
      ===============
      ===============

      ! The scheme is done 2x2 with an iterative scheme on top as we do
      ! not expect that a simple sequence of 2x2 rotations will
      ! suffice if carried out only once. Maxit=max. nr. of iterations
      do iter=1,maxit
      ttempmat=0.0
      L_old=L_index
      ! We go step by step over all unique combinations i,k with k<>i
      do i=startno,num_orb
      do k=i+1,num_orb
          ttrans=0.0
          rotorii=0.0D0
          rotorki=0.0D0
          rotorkk=0.0D0
          do atom=1,num_atoms
              aimsmat(atom,i,i)=dsqrt(occ(i)*occ(i))*taimsmat(atom,i,i)
              aimsmat(atom,i,k)=dsqrt(occ(i)*occ(k))*taimsmat(atom,i,k)
              aimsmat(atom,k,i)=dsqrt(occ(k)*occ(i))*taimsmat(atom,k,i)
              aimsmat(atom,k,k)=dsqrt(occ(k)*occ(k))*taimsmat(atom,k,k)
          enddo

          ! Here is where the theoretical notes get VERY handy
          nomin=0.0
          denomin=0.0
          do atom=1,num_atoms
              nomin=nomin+4.0*aimsmat(atom,i,k)*(aimsmat(atom,i,i)-aimsmat(atom,k,k))
              denomin=denomin+(aimsmat(atom,i,i)-aimsmat(atom,k,k))**2.0 &
              -4.0*aimsmat(atom,i,k)**2.0
          enddo
      enddo

enddo
\end{verbatim}
! And now work out the angle. In general it is computed via the tan() but we need to make sure that no terms are zero (see notes).

! Scenario 1: both the nominator and denominator are very, very small

if ((abs(denomin).lt.small).and.(abs(nomin).lt.small)) then
    alpha=0.0
endif

! Scenario 2: In the gradient only a sine remains
else if (abs(denomin).gt.(bigratio*abs(nomin))) then
    alpha=0.0
    ! This checks the derivative, we want to be on a maximum for localized orbitals and a minimum for delocalized orbitals
    if ((-4.0*cos(4.0*alpha)*denomin).gt.0) alpha=alpha+PI/4.0
    ! Maximal localization
    if (denomin.lt.0) alpha=alpha+PI/4.0
    ! Maximal delocalization
endif

! Scenario 3: In the gradient only a cosine remains
else if (abs(nomin).gt.(bigratio*abs(denomin))) then
    alpha=PI/8.0
    ! This checks the derivative, we want to be on a maximum for localized orbitals and a minimum for delocalized orbitals
    if ((-16.0*sin(4.0*alpha)*nomin).gt.0) alpha=alpha+PI/4.0
    ! Maximal localization
    if (nomin.lt.0) alpha=alpha+PI/4.0
    ! Maximal delocalization
endif

else
    ! Scenario 4: General case, we need a tangens
    alpha=0.25*datan(nomin/denomin)
    ! This checks the derivative, we want to be on a maximum for localized orbitals and a minimum for delocalized orbitals
    ! Maximal localization
    if ((-4.0*dcos(4*alpha)*denomin-16.0*dsin(4.0*alpha)*nomin).gt.0.0) &
       alpha=alpha+PI/4.0
    ! Maximal delocalization
    if ((-4.0*cos(4*alpha)*denomin-16.0*sin(4.0*alpha)*nomin).lt.0.0) &
       alpha=alpha+PI/4.0
endif

rotorii=dcos(alpha)
rotorik=dsin(alpha)
rotorki=-dsin(alpha)
rotorkk=dcos(alpha)

! Now we rotate the orbitals to get the new AOM
newocc=occ
newocc(i)=occ(i)*rotorii**2.0D0*sum(taimsmat(:,i,i))+&
B.1 THE DAFH CODE

```
occ(k)*rotorik**2.0D0*sum(taimsmat(:,k,k))+&
2.0D0*sqrt(occ(i)*occ(k))*rotorii*rotorik*sum(taimsmat(:,i,k))
newocc(k)=occ(i)*rotorki**2.0D0*sum(taimsmat(:,i,i))+&
occ(k)*rotorkk**2.0D0*sum(taimsmat(:,k,k))+&
2.0D0*sqrt(occ(i)*occ(k))*rotorkk*rotorki*sum(taimsmat(:,k,i))
```

!-----------------------------------------------------------------------------
! ttrans/trf used in subsroutine mo_transf (no need for commenting if
! formatted checkpoint file is not provided).
! Constructing the elements of the transformation matrix of the MO
! coefficients in full analogy to the AOM rotation matrix.

```
do m=1, num_orb
   ttrans(m,m)=1
enddo
```

```
ttrans(i,i)=dsqrt(occ(i)/newocc(i))*rotorii
```

```
ttrans(i,k)=dsqrt(occ(k)/newocc(i))*rotorik
```

```
ttrans(k,i)=dsqrt(occ(i)/newocc(k))*rotorki
```

```
ttrans(k,k)=dsqrt(occ(k)/newocc(k))*rotorkk
```

```
if(k.eq.startmo+1) then
   temptrans=ttrans
else
   tempmat=0.0
   do m=1, num_orb
      do n=1, num_orb
         do o=1, num_orb
            tempmat(m,n)=tempmat(m,n)+ttrans(m,o)*temptrans(o,n)
         enddo
      enddo
   enddo
   temptrans=tempmat
endif
```

```
! write(16,*) " U(i,k)" , i, k
```

```
! write(16,'(F11.7,F11.7)') rotorii,rotorik
```

```
! write(16,'(F11.7,F11.7)') rotorki,rotorkk
```

```
! write(16,*) " T(i,k)" , i, k
```

```
! do n=1,num_orb
!    write(16,'(1000F11.7)') (ttrans(n,m),m=1,num_orb)
! enddo
```

```
! if(k.eq.startmo+1) then
!    temptrans=ttrans
!else
!    tempmat=0.0
!    do m=1, num_orb
!       do n=1, num_orb
!          do o=1, num_orb
!             tempmat(m,n)=tempmat(m,n)+ttrans(m,o)*temptrans(o,n)
!          enddo
!       enddo
!    enddo
!    temptrans=tempmat
!endif
```

```
! write(16,*) " product T(i,k)" , i, k
```

```
! do m=1,num_orb
!    write(16,'(1000F11.7)') (temptrans(n,m),m=1,num_orb)
! enddo
```

```
! write(16,*)
```

```
97
```
newmat = taimsmat

do atom = 1, num_atoms
    do n = 1, num_orb
        newmat(atom, i, m) = taimsmat(atom, i, m) * dsqrt(occ(i) / newocc(i)) * rotorii &
        + taimsmat(atom, k, m) * dsqrt(occ(k) / newocc(i)) * rotorik &
        + taimsmat(atom, k, m) * dsqrt(occ(k) / newocc(k)) * rotorkk
        newmat(atom, k, m) = taimsmat(atom, i, m) * dsqrt(occ(i) / newocc(k)) * rotorki &
        + taimsmat(atom, k, m) * dsqrt(occ(k) / newocc(k)) * rotorkk
        newmat(atom, m, i) = newmat(atom, i, m)
        newmat(atom, m, k) = newmat(atom, k, m)
    enddo
enddo

! We also need to update the AOM elements

taimsmat = newmat
occ = newocc

enddo
enddo

! multiply up the single transformation matrices

if (iter.eq.1) then
    trf = temptrans
else
    tempmat = 0.0
    do i = 1, num_orb
        do j = 1, num_orb
            do k = 1, num_orb
                tempmat(i, j) = tempmat(i, j) + temptrans(i, k) * trf(k, j)
            enddo
        enddo
    enddo
end
! Compute the new localization index
call local(newmat,newocc,num_atoms,num_orb,L_index)
write(16,'(2X,A40,I6,10XF10.7)') 'Current iteration and localization index',
iter,L_index

! Did we find convergence ?
if (abs(L_index-L_old).lt.conver) then
  write(16,*) "===============================================================================
  > Convergence after ",iter," iterations"
  "Final localization index: ",L_index
  "="
  ! write(16,*)
  ! write(16,*) "***********************************************
  ! transformation matrix"
  do i=1,num_orb
    write(16,'(1000F11.7)') (trf(i,j),j=1,num_orb)
  enddo
  ! write(16,*) "***********************************************
  ! write(16,*)
  ! ! If so, we print the AOM
  if(printflag) then
    write(16,*)
    write(16,*) "newocc
    "
    write(16,'(5E16.8)') (2*newocc(j),j=1,num_orb)
    write(16,*) "new AOMs
  "
  if(printflag) then
    write(16,*) "="
    ! write(16,*)
    ! write(16,*) "***********************************************
    ! transformation matrix"
    do i=1,num_orb
      write(16,'(1000F11.7)') (trf(i,j),j=1,num_orb)
    enddo
    ! write(16,*) "***********************************************
    ! write(16,*)
    ! write(16,*) "="
    ! write(16,*) "new AOMs
  "
endif
B APPENDIX

```fortran
    do atom=1,num_atoms
        write(16,'(I8)') atom
        do j=1,num_orb
            write(16,'(1000F11.7)') (taimsmat(atom,j,l),l=1,num_orb)
        enddo
    enddo
write(16,*) "-----

    if(printflag) then
        write(16,'("␣␣␣␣TOTAL␣SUM␣OF␣AOMs")')
    endif
    do j=1,num_orb
        do l=1,num_orb
            totmat(j,l)=0.0
            do atom=1,num_atoms
                totmat(j,l)=totmat(j,l)+taimsmat(atom,j,l)
            enddo
        enddo
    enddo
    if(printflag) then
        write(16,'(1000F11.7)') (totmat(j,l),l=1,num_orb)
    endif
enddo
write(16,*) "-----

    ! comment call to subroutine if formatted checkpoint file not provided
    ! check isoflag to perform isopycnic transformation or not
    if(isoflag) then
        call mo_transf(iter)
    endif
exit
endif
```

100
B.1 THE DAFH CODE

enddo
end subroutine isopycnic

subroutine local(tempmat, tempocc, num_atoms, num_orb, L)
! subroutine to refresh the localization index each iteration
implicit none

INTEGER::i
INTEGER::atom
INTEGER::num_atoms, num_orb
REAL*8::L
REAL*8,DIMENSION(num_atoms, num_orb, num_orb)::tempmat
REAL*8,DIMENSION(num_orb)::tempocc

L=0.0
do atom=1, num_atoms
  do i=1, num_orb
    L=L+(tempocc(i)*tempmat(atom,i,i))**2.0
  enddo
enddo
return
end subroutine local

!******************************************************************************
!MO COEFFICIENTS TRANSFORMATION
!******************************************************************************
subroutine mo_transf(iter)
! subroutine to transform the MO coefficients simultaneously to
! the isopycnic transformation of the AOMs
USE dafh_data
implicit none
INTEGER::i,j,k,l,x,iter,temp_coeff
REAL*8,DIMENSION(num_bsftot, num_bsftot)::tempmat

if(iter.eq.0) then
  tempmat=0.0
  do i=1, num_bsftot
    tempmat(i,i)=1.0
  enddo
  do i=1, num_orb
    do j=1, num_orb
      tempmat(i,j)=diagmat(i,j)
    enddo
  enddo
  do j=1, num_bsftot
    enddo
  enddo
end subroutine mo_transf
B APPENDIX

do i=1,num_bsftot
do k=1,num_bsftot
c2(i,j)=c2(i,j)+tempmat(k,j)*coeff(i,k)
enddo
dodo
c2=0.0
tempmat=0.0
do i=1, num_bsftot
tempmat(i,i)=1.0
dodo
do i=1, num_orb
do j=1, num_orb
tempmat(i,j)=trf(i,j)
dodo
dodo
do j=1,num_bsftot
do i=1, num_bsftot
do k=1,num_bsftot
c2(i,j)=c2(i,j)+tempmat(j,k)*coeff(i,k)
enddo
dodo
c2=0.0
tempmat=0.0
do i=1, num_orb
do j=1, num_orb
tempmat(i,j)=trf(i,j)
dodo
dodo
c2=0.0
tempmat=0.0
dodo
dodo
c2=0.0
tempmat=0.0
dodo
dodo
endif
dend subroutine mo_transf

doint::istat,atom
integer::i,j
integer::i,j
character(90)::line
character(90)::newfile
real*8,dimension(num_bsftot)::fchk_occ
B.1 THE DAFH CODE

940  fchk_occ=0.0
941
942  if(isoflag) then
943    do i=1, num_orb
944      fchk_occ(i)=newocc(i)
945    enddo
946  else
947    do i=1, num_orb
948      fchk_occ(i)=occ_noiso(i)
949    enddo
950  endif
951
952  if(nolflag) label_lower = "all"
953
954  open (14,file=trim(fchkfile),status="old",access="sequential",IOSTAT=istat)
955  if(isoflag) then
956    write(newfile, '(A)') trim(fchkname)//"_dafh_"//trim(label_lower)//".fchk"
957  else
958    write(newfile, '(A)') trim(fchkname)//"_dafh-noiso_"//trim(label_lower)//".fchk"
959  endif
960  open (UNIT=15,file=newfile,IOSTAT=istat)
961  do
962    read(14,'(A90)',IOSTAT=istat) line
963    if(istat/=0) exit
964    if (line(1:15).eq."Number␣of␣basis") then
965      if(lindepflag) then
966        write (15,'("Number␣of␣basis␣functions␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣␣I",I17)') num_bsf
967      else
968        write (15,'(A90)') line
969      endif
970    elseif (line(1:22).eq."Alpha␣Orbital␣Energies") then
971      ! if(lindepflag) then
972      !    write (15,'("Alpha Orbitals Energies R N="',I12)') num_bsf
973      !     do i=1,int((num_bsf-1)/5)+1
974      !       read (14,*)
975      !     enddo
976      !   endif
977    elseif (line(1:15).eq."Alpha␣MO␣coeffi") then
978      ! if(lindepflag) then
979      !    write (15,'("Alpha MO coefficients R N="',I12)') num_bsf
980      !     do i=1,int((num_bsf-1)/5)+1
981      !       read (14,*)
982      !     enddo
983      !   endif
984    elseif (line(1:15).eq."Alpha␣MO␣coeffi") then
985      ! if(lindepflag) then
986      !    write (15,'("Alpha MO coefficients R N="',I12)') num_bsf
987      !     do i=1,int((num_bsf-1)/5)+1
988      !       read (14,*)
989      !     enddo
990      !   endif
! write (15,'(5E16.8)') ((coeff(i,j),i=1,num_bsftot),j=1,num_bsftot)

! do i=1,int((num_bsf*num_bsftot-1)/5)+1
! read (14,*)
! enddo
!
! else
! 
! write (15,'("Alpha_MO_coefficients_RN",I12)') num_bsf*num_bsftot
! write (15,'(5E16.8)') ((coeff(i,j),i=1,num_bsftot),j=1,num_bsf)
! do i=1,int((num_bsf*num_bsftot-1)/5)+1
! read (14,*)
! enddo
!
! endif

else

if(istat.eq.0) write (15,'(A90)') line
endif
end do
close(14)
close(15)

end subroutine write_fchk

**************************************************************************
!FUNCTIONS FOR DECAPITALIZING/CAPITALIZING STRINGS
**************************************************************************

function decapitalize(strIn) result(strOut)
% Adapted from http://www.star.le.ac.uk/~cgp/fortran.html (25 May 2012)
% Original author: Clive Page
implicit none
character(len=*) , intent(in) :: strIn
character(len=len(strIn)) :: strOut
integer :: i, j

do i = 1, len(strIn)
  j = iachar(strIn(i:i))
  if (j>= iachar("A") .and. j<=iachar("Z") ) then
    strOut(i:i) = achar(iachar(strIn(i:i))+32)
  else
    strOut(i:i) = strIn(i:i)
  end if
end do

end function decapitalize

function capitalize(strIn) result(strOut)
% Adapted from http://www.star.le.ac.uk/~cgp/fortran.html (25 May 2012)
% Original author: Clive Page
implicit none
character(len=*) , intent(in) :: strIn
character(len=len(strIn)) :: strOut
integer :: i, j

do i = 1, len(strIn)
  j = iachar(strIn(i:i))
  if (j>= iachar("A") .and. j<=iachar("Z") ) then
    strOut(i:i) = achar(iachar(strIn(i:i))+32)
  else
    strOut(i:i) = strIn(i:i)
  end if
end do

end function capitalize
B.1 THE DAFH CODE

```
character(len=len(strIn)) :: strOut
integer :: i, j

do i = 1, len(strIn)
  j = iachar(strIn(i:i))
  if (j>=iachar("a") .and. j<iachar("z") ) then
    strOut(i:i) = achar(iachar(strIn(i:i))-32)
  else
    strOut(i:i) = strIn(i:i)
  end if
end do

end function capitalize

!**************************************************************************
!RANDOM NUMBER GENERATOR
!**************************************************************************
subroutine init_random_seed()

INTEGER :: i, n, clock
INTEGER, DIMENSION(:), ALLOCATABLE :: seed

CALL RANDOM_SEED(size = n)
ALLOCATE(seed(n))

CALL SYSTEM_CLOCK(COUNT=clock)
seed = clock + 37 * (/ (i - 1, i = 1, n) /)
CALL RANDOM_SEED(put = seed)
DEALLOCATE(seed)
end
```
Appendix

C.1 TOOL FOR INCORPORATION OF EFFECTIVE CORE DENSITIES FOR THE QTAIM INTEGRATION

```
program trf_wfx
  implicit none
  INTEGER::istat
  INTEGER::i,j,x
  INTEGER::num_orb,num_el,num_alpha,num_prim,num_edf,num_tot
  INTEGER::charge,core
  INTEGER,DIMENSION(:),ALLOCATABLE::prim_centers,prim_types
  REAL*8,DIMENSION(:),ALLOCATABLE::expo,edf_coeff
  REAL*8,DIMENSION(:,:),ALLOCATABLE::coeff
  CHARACTER(90)::line,title
  CHARACTER(90)::newfile
  CHARACTER(90)::wfxfile,wfxname
  CHARACTER(10)::str
  CHARACTER(5)::str5

  call getarg(1,wfxfile)

  x = len(trim(wfxfile)) - 4
  wfxname = wfxfile(1:x)

  open (14,file=trim(wfxfile),status="old",access="sequential",IOSTAT=istat)
  core = 0
  do
    read(14,'(A90)',IOSTAT=istat) line
    if(istat/=0) exit
    if (line(1:14).eq."<Number␣of␣Occ") then
      read(14,*) num_orb
```

107
C APPENDIX

30  num_orb = num_orb + 1
31  elseif (line(1:15).eq."<Number_of_Core") then
32      read(14,*).core
33  elseif (line(1:15).eq."<Number_of_Prim") then
34      read (14,*) num_prim
35  elseif (line(1:14).eq."<Number_of_EDF") then
36      read (14,*) num_edf
37      num_tot = num_prim + num_edf
38      exit
39  endif
40  enddo
41  close(14)
42  if (core.eq.0) then
43    write(*,*) ">>> no ECP in this wfx file"
44    call exit(1)
45  endif
46
47  allocate(prim_centers(num_tot))
48  allocate(prim_types(num_tot))
49  allocate(expo(num_tot))
50  allocate(coeff(num_orb,num_tot))
51  allocate(edf_coeff(num_tot))
52  prim_centers=1
53  prim_types=1
54  expo=0.0
55  coeff=0.0
56  edf_coeff=0.0
57
58  open (14,file=trim(wfxfile),status="old",access="sequential",IOSTAT=istat)
59  do
60    read(14,'(A90)',IOSTAT=istat) line
61    if (istat/=0) exit
62    if (line(1:13).eq."<Number_of_El") then
63      read(14,*) num_el
64      num_el = num_el + core
65    elseif (line(1:15).eq."<Primitive_Cent") then
66      read(14,'(5I20)') (prim_centers(i),i=1,num_prim)
67    elseif (line(1:16).eq."<Primitive_Types") then
68      read(14,'(5I20)') (prim_types(i),i=1,num_prim)
69    elseif (line(1:14).eq."<Primitive_Exp") then
70      read(14,'(5E20.12)') (expo(i),i=1,num_prim)
71    elseif (line(1:18).eq."<EDF_Primitive_Exp") then
72      read(14,'(5E20.12)') (expo(i),i=num_prim+1,num_tot)
73    elseif (line(1:20).eq."<EDF_Primitive_Coeff") then
74      read(14,'(5E20.12)') (edf_coeff(i),i=num_prim+1,num_tot)
75    elseif (line(1:23).eq."<Molecular_Orbital_Prim") then
76      do i=1, num_orb-1
77        read(14,*)
78      read(14,*)
C.1 CORE DENSITY TOOL

80      read(14,*)
81      read(14, '(4E20.12)') (coeff(i,j),j=1,num_prim)
82      enddo
83      exit
84      endif
85      enddo
86      close(14)
87
88      open (14,file=trim(wxfname),status="old",access="sequential",IOSTAT=istat)
89      write(newfile, '(A)') trim(wfxname)//"_ecp-mo.wfx"
90      open (UNIT=15,file=newfile,IOSTAT=istat)
91      do
92          read(14,'(A90)',IOSTAT=istat) line
93          if(istat/=0) exit
94          if(line(1:7).eq."<Title>") then
95              read(14,*)
96              write(15,'(A90)') line
97              write(str5,'(I5)') core
98              write(15,'(XA)') adjustl("ECP-MO:"//str5//"␣core␣electrons␣(source␣file␣"//
99              trim(wxfname)//")")
100             elseif (line(1:14).eq."<Number␣of␣Occ") then
101                read(14,*)
102                write(15,'(A90)') line
103                write(str,'(I5)') num_orb
104                write(15,'(XA)') adjustl(str)
105             elseif (line(1:13).eq."<Number␣of␣El") then
106                  read(14,*)
107                  write(15,'(A90)') line
108                  write(str,'(I5)') num_el
109                  write(15,'(XA)') adjustl(str)
110             elseif (line(1:16).eq."<Nuclear␣Charges") then
111                  read(14,*)
112                  write(15,'(A90)') line
113                  write(str,'(I5)') 0
114                  write(15,'(XA)') adjustl(str)
115             elseif (line(1:15).eq."<Number␣of␣Core") then
116                  read(14,*)
117                  write(15,'(A90)') line
118                  write(str,'(I5)') num_el/2
119                  write(15,'(XA)') adjustl(str)
120             elseif (line(1:16).eq."<Nuclear␣Charges") then
121                  read(14,*)
122                  write(15,'(A90)') line
123                  write(str,'(I5)') 0
124                  write(15,'(XA)') adjustl(str)
125             elseif (line(1:16).eq."<Nuclear␣Charges") then
126                  read(14,*)
127                  write(15,'(A90)') line

109
write(15,'(2X)') '5.3000000000000000e+01'
elseif (line(1:15).eq."<Number of Prim") then
  read (14,*)
  write(15,'(A90)') line
  write(str,'(I5)') num_tot
  write(15,'(XA)') adjustl(str)
elseif (line(1:15).eq."<Primitive Cent") then
  write(15,'(A90)') line
  write(15,'(5I20)') (prim_centers(i),i=1,num_tot)
  do i=1,int((num_prim-1)/5)+1
     read (14,*)
  enddo
endif (line(1:15).eq."<Primitive Types") then
  write(15,'(A90)') line
  write(15,'(5I20)') (prim_types(i),i=1,num_tot)
  do i=1,int((num_prim-1)/5)+1
     read (14,*)
  enddo
elseif (line(1:14).eq."<Primitive Exp") then
  write(15,'(A90)') line
  write(15,'(5E20.12)') (expo(i),i=1,num_tot)
  do i=1,int((num_prim-1)/5)+1
     read (14,*)
  enddo
endif (line(1:14).eq."<Additional El") then
  do i=1, 12; read(14,*); enddo
  do i=1,4*(int((num_edf-1)/5)+1)
     read (14,*)
  enddo
elseif (line(1:23).eq."</Molecular Orbital Occ") then
  write(15,'(5E20.12)') real(core)
  write(15,'(A90)') line
elseif (line(1:22).eq."</Molecular Orbital En") then
  write(15,'(5E20.12)') 0.0
  write(15,'(A90)') line
elseif (line(1:24).eq."</Molecular Orbital Spin") then
  write(15,'(XA)') "Alpha, and Beta"
  write(15,'(A90)') line
elseif (line(1:23).eq."<Molecular Orbital Prim") then
  write(15,'(A90)') line
  do i=1, num_orb-1
     write(15,'(4E20.12)') (coeff(i,j),j=1,num_tot)
  enddo
write(15,'(A)') "<MO_Number>"
write(str,'(I5)') num_orb
write(15,'(XA)') adjustl(str)
write(15,'(A)') "<MO_Number>"
write(15,'(4E20.12)') (edf_coeff(i),i=1,num_tot)
else
if(istat.eq.0) write (15,'(A90)') line
endif
enddo
close(14)
close(15)
end program trf_wfx
Bibliography


BIBLIOGRAPHY


BIBLIOGRAPHY


[99] H. Pinto de Magalhães, MA thesis, ETH Zürich, Zürich, 2011.


BIBLIOGRAPHY

