The International Union of Crystallography (IUCr)’s Sagamore XIX – 2018 Conference on Quantum Crystallography (QCr)

Programme & Book of Abstracts

Sagamore 2018 Honors the Work of:
Robert Farrell Stewart (1936–2015)
& Philip Coppens (1930–2017)

IUCr Commission on Quantum Crystallography (Formerly: Commission on Charge, Spin & Momentum Densities)
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Book Editor:  C. F. Matta
Consultant:  Paul W. Ayers
Book Compiling:  Kerri AlSaidi
Copy Editor:  Lisa Cochrane
Proof Reading:  Sherry Bailey
Book Cover Art & Sagamore 2018 Logo Design:  C. F. Matta
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Chair’s Welcome to Canada & to Sagamore 2018!

Mount Saint Vincent University in Nova Scotia, Canada, is proud to host this year’s Sagamore XIX Conference of the International Union of Crystallography’s (IUCr) Commission of Quantum Crystallography (CQCr). The conference’s venue is the Halifax Convention Center (HCC), recently built in the vibrant downtown of Halifax, Nova Scotia’s Capital city.

Sagamore began in 1964 as an international conference dedicated to the study of electron charge, spin and, later, momentum densities.

Canada played host to the 1979 Sagamore conference in Mont Tremblant, Québec, as well as welcoming the 1997 Sagamore in Saskatchewan’s Prince Albert National Park’s Waskesiu Lake. Sagamore, thus, returns to Canada after 21 years! Welcome back to Canada, Sagamore, and welcome to Sagamore and to Canada, my fellow “Sagamorians”!

Bienvenue au Canada!

Sagamore 2018, your conference, lives up, thanks to you, to its international tradition and reputation. You, nearly eighty registered participants, hail from Australia, Canada, China, Colombia, Croatia, Cuba, France, Germany, Hong Kong, India, Italy, Japan, Mexico, Poland, Russia, Slovak Republic, Spain, Switzerland, UK, and the USA – and if we include national origins as well, you may add Bangladesh, Greece, Egypt, Iran, South Korea, Ukraine, and Vietnam to the list. Thus, this year’s Sagamorians come from 27 countries representing all six (populated) continents of the globe (skipping only Antarctica)

A BIG WELCOME from me to you all on behalf of my co-Chair, Prof. Paul W. Ayers, and on behalf of the entire Organization Team.

I wish to thank you all for making this event possible through your participation; for bringing your science, sense of humour, and friendship along with the ever-present open mindedness we all continue to enjoy at Sagamore conferences.

I wish to thank the present and past Members & Consultants of the IUCr - CQCr, and our discussion leaders, Dr. Carlo Gatti, Prof. Enrique Espinosa, Prof. Dylan Jayatilaka, Prof. Piero Macchi, and Prof. Masaki Takata. Each of you have agreed to come – while

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traveling great distances - to lead the round table discussions on the science of Quantum Crystallography and its policy, work that will no doubt have an influence in shaping the future of this scientific undertaking.

Following a conference as great as the 2015 Sagamore XVIII in Sardinia, Italy, is daunting at the very least. However, the passing of the torch could not have been more gracious. Our previous Sagamore Chair, Dr. Carlo Gatti, has been extremely generous with his information, sharing advice, insights, and direct help at every stage of the organization of the Halifax conference.

Thank you Carlo!

The Organization Team has also benefitted immensely from the experience and knowledge so kindly shared with us by Prof. Piero Macchi, the outgoing Chair of the Commission, and by Prof. Jean-Michel Gillet, its current Chair since 2017.

Prof. Claude Lecomte and Prof. Lou Massa have both been instrumental in helping us with their crucial suggestions and recommendations, thoughts, ideas, and also in establishing numerous key contacts indispensable for the planning of our event.

Many thanks Piero, J-M, Claude, and Lou!

Since Sagamore 2015 (XVIII), our community has lost two of its giants: Prof. Robert Farrell Stewart (1936 – 2015) and Prof. Philip Coppens (1930 – 2017). The Chair, co-Chair, and the entire Sagamore 2018 Organization Team humbly dedicate this conference in honour of Professor Stewart’s and Professor Coppens’ monumental work and contribution to the field.

Obituary tributes to Bob and Philip have appeared in *Acta Cryst. A*, and are reproduced here in full with the IUCr’s and the authors’ permissions (Professor Mark A. Spackman, and Professor Pierre Becker, respectively). We are grateful to Mark, Pierre, and the IUCr for allowing us to reproduce these obituaries.

Another important tribute to Philip, originally a festschrift turned into a memorial issue, appears in the form of a special issue of *Acta Cryst. B* (August 2017). This special issue, to which many of you have contributed invited articles, was edited by Profs. Claude Lecomte, Jason Benedict, and Yu-Sheng Chen and is entitled “Special issue on charge density, photocystallography and time-resolved crystallography: a tribute to Professor Philip Coppens”.

In Hyderabad, India, in August 2017, the IUCr’s General Assembly approved the
renaming of its “Commission on Charge, Spin, and Momentum Densities” to “Commission on Quantum Crystallography”.

There have been a number of recent meetings reflecting the growing interest in Quantum Crystallography (QCr). For example, the CECAM Discussion Meeting: Quantum Crystallography: Current Developments and Future Perspectives in 2017, organized by Dr. Alessandro Genoni and Prof. Simon Grabowsky; and the Erice School of Crystallography 2018: 52nd Course: Quantum Crystallography, organized by Prof. Piero Macchi and Prof. Dylan Jayatilaka.

A number of journals’ special issues and articles centred on QCr have also recently appeared. Examples include a festschrift in *Struct. Chem.* (issue of October 2017) honoring Professor Lou Massa, two special issues of *J. Comput. Chem.* (co-edited by Lou and I in 2018), a recent multi-author article in the press of *Chem. Eur. J.* led by Ale and Simon, and a Wikipedia article - all on the topic of the Commission’s “namesake”.

Consistently with the emerging view from these venues, Sagamore 2018 attempts to embrace neighbouring and related disciplines under its QCr umbrella. The strong participation of pioneers from the molecular imaging, laser-molecule interaction, and confined quantum systems communities exemplify a step in this direction at Sagamore 2018. It is noteworthy that at least two of these pioneers have made early and lasting contributions to the study of the topology and the 3D topography of the electron density “à la QTAIM, in modern parlance” before eventually leading the cutting edge of theory of the interaction between molecules and intense laser fields, coherent control of chemical reactivity, and orbital imaging. QCr is hoped to be the crystallization seed that attracts neighbouring disciplines opening unforeseen new horizons for all of us.

The impetus of the name-change to CQCr coincides with the Sagamore 2018 Organizing Team’s initiative of instating two International Prizes to encourage and reward excellence and healthy competition in our community.

One of these two new prizes is awarded to an established scientist at the peak of his/her career. This award is given in the name of Professor Richard F. W. Bader (1931 - 2012), who was one of the most influential theorists of the electron density with a legacy including the Quantum Theory of Atoms in Molecules (QTAIM).

The second prize is intended to reward early career brilliance, which reflects the brilliance of the prize’s namesake, the late Professor Miguel A. Blanco (1969 – 2010). I thank Prof. Víctor Luaña for his touching personal and scientific account of the life and

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* Biographical notes on both prizes namesakes, M. A. Blanco and R. F. W. Bader can be found within the biographical section (starting at p. 147).
work of Miguel (p. 148).

To ensure both fairness and independence of the selection process for these two prizes, my co-Chair and I kept our maximal distance from the prize committees, the nomination and selection process, and the voting, all of which were strictly confidential. Only once the final decisions were made did the committees’ chairs share the competition results with my co-Chair, Prof. Ayers, and myself.

The Bader Prize committee was chaired by Dr. James Britten and the Blanco Prize was chaired by Dr. Carlo Gatti.

I thank both Jim and Carlo and the members of their respective committees for their time and careful evaluation of the submitted nominations. I note in passing that self-nominations were allowed in addition to the standard nomination by others.

As Chair of Sagamore 2018, I was informed that the competition for both prizes this year was stiff. I have already announced the names of the 2018 winners by email, and judging from the replies I have received to date, the QCr/Sagamore community appears to be very satisfied and happy with both choices.

It is with the greatest pleasure, and on behalf of Prof. Paul W. Ayers and of the entire Organization Team, that I warmly congratulate:

Prof. Paul L. A. Popelier

for winning the (Inaugural) 2018 Richard F. W. Bader International Prize for Excellence in Electron Density Research: “for his exceptional contributions in the development of pure and applied Quantum Chemical Topology (QCT)”;

and

Dr. Eduard Matito i Gras

for winning the 2018 Miguel A. Blanco International Prize for Early Career Work in Charge Density: “for his original and outstanding contributions in the development of new quantum mechanical methods and of new descriptors of chemical behaviour based on the electron and electron pair density distributions”.

Sagamore 2018 has been generously supported, both financially and administratively, by the local hosting organization, Mount Saint Vincent University (MSVU, or “The Mount”, as we commonly call it here). We have also benefited from the largesse of other generous donors/sponsors, all of whom are acknowledged on a page of this book devoted to that purpose and elsewhere. I wish to single out here Mr. Jeff Turner, Sales
Director, Discover Halifax (one of our sponsors), for his incredible help and support especially in the early planning phases of Sagamore 2018 – help that he continues to offer until today. Thank you Jeff for all the ideas and help you provided and continue to provide!

In this regard, I acknowledge with much gratitude the invaluably strong support of MSVU current and former Presidents and Vice-Chancellors Dr. Mary Bluechardt and Dr. Ramona Lumkin; MSVU Vice President and Provost Dr. Elizabeth Church; MSVU Associate VP - Research Dr. Gayle MacDonald; and my Dean of Arts and Science, Dr. Brook Taylor.

The prospect of the success of Sagamore 2018 rests in large part due to the work of the core event Planning and Organization Team, led by our Finance Manager Ms. Cathleen Madgett, Event Manager Ms. Lisa Cochrane and our Administrative Assistant Ms. Kerri AlSaidi, who put together this book of Abstracts, and Website Administrator Mr. Paul Lindgreen. Proof reading and revision was undertaken by Ms. Sherry Bailey whom I thank profusely. I also wish to thank our wonderful student volunteer team: Ms. Tammy Lauritsen, Mr. Lázaro A. Monteserín Castanedo, and Mr. Youji Cheng.

Thank you so much Lisa, Cathleen, Kerri, Paul, Tammy, Lázaro, and Youji! Everyone appreciates your creative efforts and really great work.

In closing, I wish you all a very pleasant stay in Halifax, the capital city of the wonderful Canadian Province of Nova Scotia, and an intellectually rich and rewarding experience at Sagamore 2018.

We welcome you with open arms!

Chérif F. Matta
Chair of Sagamore 2018
Member of the IUCr Commission on Quantum Crystallography
Professor and Chair
Dept. of Chemistry and Physics
Mount Saint Vincent University

In person and on behalf of:
Prof. Paul W. Ayers, Co-Chair of Sagamore 2018,
and the entire Organization Team.

Halifax,
26 July 2018
We are grateful to our Sagamore 2018 Sponsors

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Sagamore 2018 Programme

Sunday - 8 July

2:00 - 5:00 pm  Registration

Walk to Sackville Landing on the waterfront, behind the Maritime Museum, at 1655 Lower Water Street, to board the Tall Ship Silva for a chartered cruise of historic Halifax Harbour.

WELCOME RECEPTION

5:30 - 7:30 pm  While enjoying scenic Halifax from the deck of a majestic ship in the harbour, greet your colleagues while enjoying local wines and hors d’oeuvres.

Monday - 9 July

9:00 - 9:10 am  Opening remarks by Conference Chair and Co-Chair

Chérif F. Matta
Paul W. Ayers

Start: 9:10 am  End: 12:00 pm

SESSION 1:

Ultrasfast science and molecular imaging

Chair:

Pierre-Nicolas Roy

9:10 - 9:20 am  Introductory remarks by Session Chair

Pierre-Nicolas Roy

Plenary:

9:20 - 10:00 am  Mapping atomic motions with ultrabright electrons: Fundamental space-time limits to imaging chemistry

R. J. Dwayne Miller

10:00 - 10:20 am  Many-electron effects in calculated laser-induced electron diffraction spectra of laser-driven molecules

T. Tung Nguyen-Dang
<table>
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<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker</th>
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<td>10:20 - 10:40 am</td>
<td>COFFEE BREAK</td>
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<tr>
<td>10:40 - 11:20 am</td>
<td>Plenary: Circular polarization in attosecond phenomena and applications</td>
<td>André D. Bandrauk</td>
<td>32</td>
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<tr>
<td>11:20 am - 12:00 pm</td>
<td>Plenary: Molecular movies from ultrafast time-resolved gas phase x-ray scattering</td>
<td>Peter M. Weber</td>
<td>33</td>
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<tr>
<td>12:00 - 1:40 pm</td>
<td>LUNCH</td>
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<tr>
<td>1:40 - 2:00 pm</td>
<td>Exploring the quantum / electron crystallography nexus</td>
<td>Philip Nakashima</td>
<td>35</td>
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<td></td>
<td><strong>END OF SESSION 1</strong></td>
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<tr>
<td><strong>SESSION 2:</strong></td>
<td>Start: 2:00 pm End: 3:50 pm</td>
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<tr>
<td>2:00 - 2:10 pm</td>
<td>Introductory remarks by Session Chair</td>
<td>Philip Nakashima</td>
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<tr>
<td>2:10 - 2:30 pm</td>
<td>Quantum effects and properties of nanoconfined molecular rotors?</td>
<td>Pierre-Nicholas Roy</td>
<td>38</td>
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<tr>
<td>2:30 - 2:50 pm</td>
<td>Nano cool, micro cooler! What do we want in our plasmonic materials, bandgap or no bandgap?</td>
<td>Vaibhav Thakore</td>
<td>39</td>
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Monday - 9 July

2:50 - 3:10 pm  
*Joint refinements on YTiO₃: State of the art and first steps to the wave functions refinement*  
Nicolas Claiser  40

3:10 - 3:30 pm  
*Donor-acceptor stabilization of, and bonding in, low oxidation state main group element hydrides*  
Alex Brown  42

3:30 - 3:50 pm  
*Novel nanocrystalline material and their application*  
Khashayar Ghandi  43

END OF SESSION 2

3:50 - 4:10 pm  
COFFEE BREAK

Start: 4:10 pm  
End: 5:40 pm  
SESSION 3:  
*Matter under extreme conditions and induced phase transitions*  
Chair: Piero Macchi

4:10 - 4:20 pm  
*Introductory remarks by Session Chair*  
Piero Macchi

4:20 - 5:00 pm  
*Plenary:*  
On the control parameters of pressure-induced bond activation/compression  
Wolfgang Scherer  44

5:00 - 5:20 pm  
*Atomic and molecular properties of diatomic molecules in external electric fields*  
Shahin Sowlati-Hashjin  46

5:20 - 5:40 pm  
*Bonding formation along the pressure-induced B3-B1 phase transition in InP*  
Jose Manuel Recio  48

END OF SESSION 3
Monday - 9 July

5:40 - 5:50 pm
Short out of sequence talk: *Pentacoordinated silicon compounds as a model system to study SN_2 reactions*
Malte Fugel

6:00 - 9:00 pm
POSTER SESSION & COCKTAIL
(INCLUDING POSTER PRIZES COMPETITION AND VOTE)

Tuesday - 10 July

<table>
<thead>
<tr>
<th>Start: 9:00 am</th>
<th>SPECIAL AWARDS SESSION</th>
<th>Chair: Carlo Gatti</th>
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<tr>
<td>End: 10:40 am</td>
<td>Remarks by the Session Chair</td>
<td>Carlo Gatti</td>
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<tr>
<td>9:00 - 9:05 am</td>
<td>Introductory remarks by the Chair of the (Early Career) Miguel A. Blanco Prize Selection Committee</td>
<td>Carlo Gatti</td>
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<tr>
<td>9:10 - 9:50 am</td>
<td>The Miguel A. Blanco Prize Lecture: The pair density as a source of chemical information</td>
<td>Eduard Matito</td>
</tr>
<tr>
<td>9:50 - 9:55 am</td>
<td>SHORT 5 MINUTES BREAK</td>
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</tr>
<tr>
<td>9:55 - 10:00 am</td>
<td>Introductory remarks by a member of the (Advanced Career) Richard F. W. Bader Prize Selection Committee</td>
<td>T. Tung Nguyen-Dang</td>
</tr>
<tr>
<td>10:00 - 10:40 am</td>
<td>The Richard F. W. Bader Prize Lecture: Topologically partitioned electron correlation energy</td>
<td>Paul L. A. Popelier</td>
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## Tuesday - 10 July

**END OF SPECIAL AWARD SESSION**

10:40 am - 11:00 am  **COFFEE BREAK**

<table>
<thead>
<tr>
<th>Start: 11:00 am</th>
<th>End: 4:40 pm</th>
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### SESSION 4:

**Advances in the theoretical and experimental studies of the electron density**

**Chair:** Wolfgang Scherer

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<td>11:00 - 11:10 am</td>
<td>Remarks by the Session Chair</td>
<td>Wolfgang Scherer</td>
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<tr>
<td>11:10 - 11:30 am</td>
<td>Electron counting in position space: From quantum fragments to Lewis structures to multicenter bond</td>
<td>Ángel Martín Pendás</td>
<td>57</td>
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<td>11:30 - 11:50 am</td>
<td>Density meets orbitals</td>
<td>Lukas Bucinsky</td>
<td>58</td>
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<tr>
<td>11:50 am - 12:00 pm</td>
<td>Short talk: X-ray charge density study of chemical bonding in ZnSb</td>
<td>Hidetaka Kasai</td>
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12:00 – 1:40 pm **LUNCH**

### SESSION 4 (Cont’d)

**Plenary:**

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<tr>
<td>1:40 - 2:20 pm</td>
<td>Electron density and real structure of materials</td>
<td>Yuri Grin</td>
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<tr>
<td>2:20 - 2:40 pm</td>
<td>Electron density from strong-correlation wave functions</td>
<td>Markus Reiher</td>
<td>62</td>
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<td>2:40 -3:00 pm</td>
<td>How do density functional approximations affect our results?</td>
<td>Julia Contreras-Garcia</td>
<td>63</td>
</tr>
<tr>
<td>Time</td>
<td>Session</td>
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</tbody>
</table>
| 3:00 - 3:20 pm | The topological structure of complex molecules: Challenges and near future directions  
              | Hugo J. Bohórquez 65                                                    |
| 3:20 - 3:40 pm | Comprehensive electron density analysis of 1 to 3D systems fully integrated in the ab initio CRYSTAL code | Silvia Casassa 67                                                      |
| 3:40 - 4:00 pm | COFFEE BREAK                                                            |
| 4:00 - 4:20 pm | Next generation QTAIM                                                   | Samantha Jenkins 69                                                    |
| 4:20 - 4:40 pm | The electron density at the complete basis set limit                   | Seyed Abdolreza Sadjadi 71                                           |

**END OF SESSION 4**

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<th>Time</th>
<th>Session</th>
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</thead>
<tbody>
<tr>
<td>4:40 - 4:50 pm</td>
<td>Remarks by the Session Chair</td>
</tr>
<tr>
<td>4:50 - 5:10 pm</td>
<td>Enzymatic reaction modelling as a stretch-test of machine learning based on small-molecule electron density topological training data</td>
</tr>
<tr>
<td>5:10 - 5:30 pm</td>
<td>The catalytic role of hydrogen bond interactions</td>
</tr>
<tr>
<td>5:30 - 5:50 pm</td>
<td>Sila-Ibuprofen and interaction densities in crystal vs. enzyme environments</td>
</tr>
</tbody>
</table>

**SESSION 5:**

Electron density in catalysis & enzymology

Chair: Julia Contreras-Garcia
**Tuesday - 10 July**

**END OF SESSION 5**

Open meeting of the IUCr’s Commission on Quantum Crystallography (CQCr)

**Wednesday - 11 July**

Start: 9:00 am
End: 2:20 pm

<table>
<thead>
<tr>
<th>Time</th>
<th>Session Activity</th>
<th>Chair</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00 - 9:10 am</td>
<td>Introductory remarks by Session Chair</td>
<td>Dylan Jayatilaka</td>
</tr>
<tr>
<td>9:10 - 9:50 am</td>
<td>Plenary: <em>In good experiments we can trust!</em></td>
<td>Dietmar Stalke</td>
</tr>
<tr>
<td>9:50 - 10:10 am</td>
<td>Libraries of extremely localized molecular orbitals and their coupling to Hirshfeld atom refinement</td>
<td>Alessandro Genoni</td>
</tr>
<tr>
<td>10:10 - 10:30 am</td>
<td>Comparison of experimental and theoretical results of electronic structure of 3-(2’-tetrahydropyranoxy)-4- methylthiazole-2(3H)-thione</td>
<td>Jozef Kožišek</td>
</tr>
<tr>
<td>10:30 am - 11:00 am</td>
<td>COFFEE BREAK</td>
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# Wednesday - 11 July

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Speaker</th>
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</thead>
<tbody>
<tr>
<td>11:00 - 11:20 am</td>
<td><em>Quantum crystallography (QCr): Early views &amp; recent ideas</em></td>
<td>Lou Massa</td>
<td>84</td>
</tr>
<tr>
<td>11:20 - 11:40 am</td>
<td>Experimental and theoretical structure factors of simple metal oxides</td>
<td>Eiji Nishibori</td>
<td>85</td>
</tr>
<tr>
<td>11:40 am - 12:00 pm</td>
<td><em>A method to estimate statistical errors of properties derived from charge density modeling</em></td>
<td>Benoît Guillot</td>
<td>88</td>
</tr>
<tr>
<td>12:00 - 1:40 pm</td>
<td>LUNCH</td>
<td></td>
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<tr>
<td>1:40 - 2:00 pm</td>
<td>Methods development for charge density studies of actinide compounds: from data reduction to model building</td>
<td>Christopher G. Gianopoulos</td>
<td>89</td>
</tr>
<tr>
<td>2:00 - 2:20 pm</td>
<td>Removing residual bond density in organic molecules: A technical note</td>
<td>Alexander Y. Nazarenko</td>
<td>90</td>
</tr>
<tr>
<td>END OF SESSION 6</td>
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</table>

**Start: 2:20 pm**

**SESSION 7:**

*Modern approaches to chemical bonding & aromaticity*

**Chair:** Ángel Martín Pendás

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Speaker</th>
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<tbody>
<tr>
<td>2:20 - 2:30 pm</td>
<td>Introductory remarks by Session Chair</td>
<td>Ángel Martín Pendás</td>
<td></td>
</tr>
<tr>
<td>2:30 - 2:50 pm</td>
<td>Evaluation of spatial domains</td>
<td>Miroslav Kohout</td>
<td>92</td>
</tr>
</tbody>
</table>
Wednesday - 11 July

2:50 - 3:10 pm  Characterizing the halogen and chalcogen bonds in crystals: PAEM vs ESP  Ekaterina Bartashevich  93

3:10 - 3:30 pm  Charge density analysis of triphosphazenes: Aromaticity and the NCl unit  Fernando Cortés-Guzmán  96

3:30 - 4:00 pm  COFFEE BREAK

4:00 - 4:20 pm  How real-space bonding indicators can help in description of the nature of donor acceptor bonds  Lilianna Chęcińska  97

4:20 - 4:40 pm  Stacking of planar polyenic rings: From dispersion interactions to multicentric two-electron covalent bonding  Krešimir Molčanov  98

4:40 - 5:00 pm  What does electron density analysis tell us about bonding in transition metal-doped boron and carbon clusters?  N. Sukumar (via video conferencing)  100

END OF SESSION 7

5:00 – 5:45 pm  Sagamore 2018 Group Photo

5:45 - 6:00 pm  TRANSIT TIME

Sagamore 2018 Banquet

(Including celebration of the Sagamore 2018 international awards laureates & announcing poster prizes winners)
### Thursday - 12 July

#### SESSION 8:
**Advanced characterization, detection, and inelastic scattering**
**Chair:** Vaibhav Thakore

<table>
<thead>
<tr>
<th>Time</th>
<th>Presentation</th>
<th>Speaker</th>
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<tbody>
<tr>
<td>9:00 - 9:10 am</td>
<td>Introductory remarks by Session Chair</td>
<td>Vaibhav Thakore</td>
</tr>
<tr>
<td>9:10 - 9:30 am</td>
<td>Spin-resolved momentum densities: What we can learn from magnetic Compton scattering</td>
<td>Jon Duffy</td>
</tr>
<tr>
<td>9:30 - 9:50 am</td>
<td>Advanced spectroscopic characterization of lithium-ion battery materials using x-ray Compton scattering</td>
<td>Hasnain Hafiz</td>
</tr>
<tr>
<td>9:50 - 10:10 am</td>
<td>Nonlinear optical microscopy for discriminating tissues based on ultrastructure</td>
<td>Danielle Tokarz</td>
</tr>
</tbody>
</table>

**END OF SESSION 8**

#### SESSION 9:
**Advanced material design and structure-to-property relationships**
**Chair:** Miroslav Kohout

<table>
<thead>
<tr>
<th>Time</th>
<th>Presentation</th>
<th>Speaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:10 - 10:20 am</td>
<td>Introductory remarks by Session Chair</td>
<td>Miroslav Kohout</td>
</tr>
<tr>
<td>10:20 - 10:40 am</td>
<td>Phonon-mediated high-temperature superconductivity?</td>
<td>Roman Krems</td>
</tr>
<tr>
<td>10:40 - 11:00 am</td>
<td>COFFEE BREAK</td>
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</tr>
<tr>
<td>11:00 - 11:20 am</td>
<td>Design of macrocyclic chelating agents with actinium for development of targeted radiotherapy</td>
<td>Amanda Morgenstern</td>
</tr>
</tbody>
</table>
Thursday - 12 July

11:20 am - 11:40 am
Structure-property relationships in an ambipolar organic semiconductor cum NLO material: New insights from energy frameworks and charge density analysis
Parthapratim Munshi

11:40 - 12:00 am
Revisiting the structure of “Pbca” (±)- [Co(en)₃]I₃.H₂O - Comparing the results obtained by x-ray and neutron diffraction with those predicted with PLATON and the flack test when using x-ray data alone
Ivan Bernal

END OF SESSION 9

12:00 - 1:40 pm
LUNCH

SESSION 10:
Chair:
Enrique Espinosa

1:40 - 1:50 am
Introductory remarks by Session Chair
Enrique Espinosa

1:50 - 2:30 pm
Long Talk:
The many faces of localization-delocalization matrices
Ronald L. Cook

2:30 - 2:50 pm
Use of differential electron density to elucidate the origins of stereoselectivity in synthetic organic reactions
Paul Ha-Yeon Cheong

END OF SESSION 10
Thursday - 12 July

2:50 - 3:10 pm
Out of sequence talk: *Half-metallicity of graphite-like and amorphous carbon nanoparticles and their potential applications in spin catalysis: Quantum chemistry predictions*

Gilles Peslherbe

3:10 - 4:45 pm
FREE TIME

EXCURSION DINNER

5:00 - 9:00 pm
Bus charter excursion to scenic Peggy’s Cove, to enjoy a walk on the majestic rocks and a light dinner at the on-site restaurant

Friday - 13 July

9:00 - 10:20 am
Round Table 1:
*Quantum Crystallography: Past, Present, and Future*

Carlo Gatti,
Enrique Espinosa,
Dylan Jayatilaka,
Piero Macchi,
Masaki Takata

10:20 - 10:40 am
COFFEE BREAK

10:40 - 12:00 am
Round Table 2:
*Experiment & Theory: Can the Synergy be Furthered?*

Carlo Gatti,
Enrique Espinosa,
Dylan Jayatilaka,
Piero Macchi,
Masaki Takata

12:00 - 12:10 am
Closing remarks from the Chair and Co-chair of Sagamore 2018

Chérif F. Matta
Paul W. Ayers

12:10 pm
ADJOURNMENT – FAREWELL
## POSTER SESSION*

**Monday – 9 July (6:00 pm – 9:00 pm)**

Posters are listed in alphabetical order by the family name of the presenting author:

<table>
<thead>
<tr>
<th>Poster number</th>
<th>Title</th>
<th>Presenting Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>On the thermodynamic stability and the natural selection of canonical nucleosides in the prebiotic evolution of life</td>
<td>Lázaro A. Monteserín Castanedo</td>
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<tr>
<td>2</td>
<td>A “direct” mechanism for the action of the genoprotectors extracted from the Cuban plant Phyllanthus Orbicularis K</td>
<td>Lázaro A. Monteserín Castanedo</td>
</tr>
<tr>
<td>3</td>
<td>Interpretation of the Kernel Energy Method (KEM) using the theory of Interacting Quantum Atoms (IQAs)</td>
<td>Youji Cheng</td>
</tr>
<tr>
<td>4</td>
<td>IP data correction for accurate charge density study</td>
<td>Yuka Deguchi</td>
</tr>
<tr>
<td>5</td>
<td>Theoretical study of electron density and energy transfer in photophysical processes</td>
<td>Jesús Hernández-Trujillo</td>
</tr>
<tr>
<td>6</td>
<td>Determination of spin and orbital moments in Nd$_2$Ir$_2$O$_7$ using magnetic Compton scattering</td>
<td>Daniel O’Neill</td>
</tr>
<tr>
<td>7</td>
<td>Total X-ray wavefunction refinement</td>
<td>Rumpa Pal</td>
</tr>
<tr>
<td>8</td>
<td>Experimentally refined density functional theory on strongly correlated materials</td>
<td>Ding Peng</td>
</tr>
</tbody>
</table>

* Two Poster Prize winners will be announced at the Conference Banquet. Winner will be selected by a voting process from the posters displayed at the poster session.
<table>
<thead>
<tr>
<th>Poster Number</th>
<th>Title</th>
<th>Author</th>
<th>Page</th>
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<tbody>
<tr>
<td>9</td>
<td>The chemistry of transition metal structure</td>
<td>Malavikha Rajivmoorthy</td>
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<td>10</td>
<td>Electron density redistribution during a photoinduced geometrical change of copper (I) complexes</td>
<td>David Ramírez- Palma</td>
<td>137</td>
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<td>11</td>
<td>Theoretical study of reactions mediated by ternary Cu(II) complexes</td>
<td>Lillian Gisela Ramírez-Palma</td>
<td>139</td>
</tr>
<tr>
<td>12</td>
<td>Pinpointing origins of selectivity with dimensionally reduced electron density</td>
<td>H. Camille Richardson</td>
<td>141</td>
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<tr>
<td>13</td>
<td>X-ray charge density study of molybdenum</td>
<td>Tomoaki Sasaki</td>
<td>142</td>
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<td>14</td>
<td>Computational investigation of polyhexamethylene biguanide (PHMB) mechanism of action on the bacterial membrane</td>
<td>Shahin Sowlati- Hashjin</td>
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<tr>
<td>15</td>
<td>Gradient bundle analysis — Full volumetric charge density behavior in a single plot</td>
<td>Tim Wilson</td>
<td>145</td>
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<tr>
<td>Paul W. Ayers</td>
<td>McMaster University Canada</td>
<td><a href="mailto:ayers@mcmaster.ca">ayers@mcmaster.ca</a></td>
<td></td>
</tr>
<tr>
<td>André D. Bandrauk</td>
<td>Université de Sherbrooke Canada</td>
<td><a href="mailto:andre.bandrauk@usherbrooke.ca">andre.bandrauk@usherbrooke.ca</a></td>
<td></td>
</tr>
<tr>
<td>Ekaterina V. Bartashevich</td>
<td>South Ural State University Russia</td>
<td><a href="mailto:bartashevichev@susu.ru">bartashevichev@susu.ru</a></td>
<td></td>
</tr>
<tr>
<td>Ivan Bernal</td>
<td>Rutgers University USA</td>
<td><a href="mailto:bernalibg@gmail.com">bernalibg@gmail.com</a></td>
<td></td>
</tr>
<tr>
<td>Hugo J. Bohórquez</td>
<td>Fundación Instituto de Inmunología de Colombia Colombia</td>
<td><a href="mailto:hugo.j.bohorquez@fidic.org.co">hugo.j.bohorquez@fidic.org.co</a></td>
<td></td>
</tr>
<tr>
<td>Alexander Brown</td>
<td>University of Alberta Canada</td>
<td><a href="mailto:alex.brown@ualberta.ca">alex.brown@ualberta.ca</a></td>
<td></td>
</tr>
<tr>
<td>Lukas Bucinsky</td>
<td>Slovak University of Technology in Bratislava Slovak Republic</td>
<td><a href="mailto:lukas.bucinsky@stuba.sk">lukas.bucinsky@stuba.sk</a></td>
<td></td>
</tr>
<tr>
<td>Silvia Casassa</td>
<td>Università degli Studi di Torino Italy</td>
<td><a href="mailto:silvia.casassa@unito.it">silvia.casassa@unito.it</a></td>
<td></td>
</tr>
<tr>
<td>Lilianna Checińska</td>
<td>Universytet Łódzki Poland</td>
<td><a href="mailto:liiiana.chechinska@chemia.uni.lodz.pl">liiiana.chechinska@chemia.uni.lodz.pl</a></td>
<td></td>
</tr>
<tr>
<td>Youji Cheng</td>
<td>Saint Mary’s University Canada</td>
<td><a href="mailto:youji.cheng@smu.ca">youji.cheng@smu.ca</a></td>
<td></td>
</tr>
<tr>
<td>Ha-Yeon (Paul) Cheong</td>
<td>Oregon State University USA</td>
<td><a href="mailto:cheongh@oregonstate.edu">cheongh@oregonstate.edu</a></td>
<td></td>
</tr>
<tr>
<td>Nicolas Claiser</td>
<td>Université de Lorraine France</td>
<td><a href="mailto:nicolas.claiser@univ-lorraine.fr">nicolas.claiser@univ-lorraine.fr</a></td>
<td></td>
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<tr>
<td>Julia Contreras-Garcia</td>
<td>CNRS &amp; Université Pierre et Marie Curie France</td>
<td><a href="mailto:julia.contreras.garcia@gmail.com">julia.contreras.garcia@gmail.com</a></td>
<td></td>
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<tr>
<td>Maria Isabel Colom</td>
<td>Oviedo Spain</td>
<td><a href="mailto:jmrecio@uniovi.es">jmrecio@uniovi.es</a></td>
<td></td>
</tr>
<tr>
<td>Ronald Cook</td>
<td>TDA Research Denver, CO</td>
<td><a href="mailto:rmlcook@gmail.com">rmlcook@gmail.com</a></td>
<td></td>
</tr>
<tr>
<td>Fernando Cortés-Guzmán</td>
<td>Universidad Nacional Autónoma de México Mexico</td>
<td><a href="mailto:fercor@unam.mx">fercor@unam.mx</a></td>
<td></td>
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<tr>
<td>Aurora Costales</td>
<td>University of Oviedo Spain</td>
<td><a href="mailto:costalesmaria@uniovi.es">costalesmaria@uniovi.es</a></td>
<td></td>
</tr>
<tr>
<td>Yuka Deguchi</td>
<td>University of Tsukuba Japan</td>
<td><a href="mailto:s1720270@s.tsukuba.ac.jp">s1720270@s.tsukuba.ac.jp</a></td>
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<td>Jonathan Duffy</td>
<td>University of Warwick UK</td>
<td><a href="mailto:j.a.duffy@warwick.ac.uk">j.a.duffy@warwick.ac.uk</a></td>
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<td>Espinosa Enrique</td>
<td>Université de Lorraine France</td>
<td><a href="mailto:enrique.espinosa@univ-lorraine.fr">enrique.espinosa@univ-lorraine.fr</a></td>
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<tr>
<td>Malte Fugel</td>
<td>University of Bremen Germany</td>
<td><a href="mailto:m.fugel@uni-bremen.de">m.fugel@uni-bremen.de</a></td>
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</table>
Krešimir Molčanov  
(Invited Speaker)  
Rudjer Bošković Institute  
Croatia  
kmolcano@irb.hr

Lazaro Monteserin-Castanedo  
(Contributed Poster)  
Mount Saint Vincent University, Saint Mary’s University, & University of Havana  
Canada & Cuba  
lamonteserincastanedo@gmail.com

Amanda Morgenstern  
(Invited Speaker)  
Los Alamos National Labs  
USA  
amorgenstern@lanl.gov

Parthapratim Munshi  
(Invited Speaker)  
Shiv Nadar University  
India

Philip Nakashima  
(Invited Speaker)  
Monash University  
Australia  
philip.nakashima@monash.edu

Alexander Y. Nazarenko  
(Invited Speaker)  
State University of New York (SUNY) - College at Buffalo  
USA  
nazareay@buffalostate.edu

Thanh-Tung Nguyen-Dang  
(Invited Speaker)  
Université Laval  
Canada  
tung@chm.ulaval.ca

Eiji Nishibori  
(Contributed Speaker)  
University of Tsukuba  
Japan  
nishibori.eiji.ga@u.tsukuba.ac.jp

Daniel O’Neill  
(Contributed Poster)  
University of Warwick  
UK  
d.o-neill.1@warwick.ac.uk

Rumpa Pal  
(Contributed Poster)  
University of Bremen  
Germany  
rpal@uni-bremen.de

Ding Peng  
(Contributed Poster)  
Monash University  
Australia  
ding.peng@monash.edu

Gilles Peslherbe  
(Invited Speaker)  
Concordia University  
Canada  
gilles.peslherbe@concordia.ca

Paul L. A. Popelier  
(Prize Winner/Honoree)  
University of Manchester  
UK  
paul.popelier@manchester.ac.uk

Malavikha Rajivmoorthy  
(Contributed Poster)  
Colorado School of Mines  
USA  
mrajivmoorthy@mymail.mines.edu

David Ignacio Ramírez Palma  
(Contributed Poster)  
Universidad Nacional Autónoma de México  
Mexico  
david.ramp49@gmail.com

Lillian Gisela Ramírez Palma  
(Contributed Poster)  
Universidad Nacional Autónoma de México  
Mexico  
lila.gis.rp@gmail.com

Jose Manuel Recio  
(Invited Speaker)  
University of Oviedo  
Spain  
jmrecio@uniovi.es

Markus Reiher  
(Invited Speaker)  
ETH-Zurich  
Switzerland  
markus.reiher@phys.chem.ethz.ch

Hannah Camille Richardson  
(Contributed Poster)  
Oregon State University  
USA  
richahan@oregonstate.edu

Pierre-Nicholas Roy  
(Invited Speaker)  
University of Waterloo  
Canada  
pnroy@uwaterloo.ca

SeyedAbdolreza Sadjadi  
(Invited Speaker)  
University of Hong Kong  
Hong Kong  
abdi1374@gmail.com

Yoshiharu Sakurai  
(Invited Participant)  
Japan Synchrotron Radiation Research Institute  
Japan  
sakurai@spring8.or.jp

Tomoaki Sasaki  
(Contributed Poster)  
University of Tsukuba  
Japan  
s1630070@u.tsukuba.ac.jp

Wolfgang Scherer  
(Plenary Speaker)  
Universität Augsburg  
Germany  
wolfgang.scherer@physik.uni-augsburg.de
Shahin Sowlati-Hashjin
(Invited Speaker / Contributed Poster)
University of Western Ontario
Canada
shahinsowlati@yahoo.com

Dietmar Stalke
(Plenary Speaker)
Georg-August-Universität
Göttingen
Germany
dstalke
@chemie.uni-goettingen.de

Ingrid Stalke
(Invited Participant)
Georg-August-Universität
Göttingen
Germany
i.stalke@gmx.de

N. Sukumar
(Invited Speaker)
Shiv Nadar University
India
n.sukumar@snu.edu.in

Masaki Takata
(Invited Discussion Leader)
University of Tokyo
Japan
masaki.takata.a4
@tohoku.ac.jp

Vaibhav Thakore
(Invited Speaker)
University of Western Ontario
Canada
vthakore@uwo.ca

Danielle Tokarz
(Invited Speaker)
Saint Mary’s University
Canada
danielle.tokarz@smu.ca

Peter M. Weber
(Plenary Speaker)
Brown University
USA
Peter_Weber@brown.edu

Tim Wilson
(Contributed Poster)
Colorado School of Mines
USA
twilson@mines.edu
Oral Presentations
Following the Programme’s Order
Mapping atomic motions with ultrabright electrons:
Fundamental space-time limits to imaging chemistry

R. J. Dwayne Miller 1, 2

1. The Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany, dwayne.miller@mpsd.mpg.de
2. Departments of Chemistry and Physics, University of Toronto, Canada

Keywords: femtosecond electron diffraction, reduced dimensionality, atomically resolved structural dynamics

One of the dream experiments in chemistry has been to watch atomic motions on the primary timescales of chemistry. This prospect would provide a direct observation of the reaction forces, the very essence of chemistry, and the central unifying concept of transition states that links chemistry to biology. This experiment has been referred to as "making the molecular movie" with respect to observing net rms atomic motions during structural changes. Due to the extraordinary requirements for simultaneous spatial-temporal resolution and brightness, it was thought to be an impossible quest and has been previously discussed in the context of the purest form of a Gedanken experiment. With the development of ultrabright electron sources capable of literally lighting up atomic motions, this experiment has been realized (Siwick et al. Science 2003). The first studies focused on relatively simple systems. Further advances in source brightness have opened up even complex organic systems and solution phase reaction dynamics to atomic inspection. A number of different chemical reactions will be discussed from electrocyclic reaction with conserved stereochemistry (Jean-Ruel et al JCP B 2013), intermolecular electron transfer for organic systems (Gao et al Nature 2013), metal to metal electron transfer (Ishikawa et al, Science 2015), to the recent observation of coherently directed bond formation using the classic I 3− system, in a process analogous to a quantum Newton’s cradle (Xian et al Nature Chem 2017). These studies have discovered that these nominally 100+ dimensional problems, representing the number of degrees of freedom in the system, distilled down to atomic projections along a few principle reaction coordinates. The most dramatic example will be shown for the first all atom resolved chemical reaction with sub-Å (.01 Å) and 100 fs timescale resolution (Ishakawa, Hayes et al, Science 2015) – the fundamental space-time resolution to following the primary processes of chemistry. At this resolution, without any detailed analysis, the key large-amplitude modes can be identified by eye from the molecular movie. This reduction in dimensionality appears to be general, arising from the very strong anharmonicity of the many body potential in the barrier crossing region. We now are beginning to see the underlying physics for the generalized reaction mechanisms that have been empirically discovered over time. The “magic of chemistry” is this enormous reduction in dimensionality in the barrier crossing region that ultimately makes chemical concepts transferrable. How far can this reductionist view be extended with respect to complexity? With further advances in space-time resolution/sensitivity, even quantum aspects will be resolvable, which will be discussed. The ultimate goal in scaling system complexity is to obtain atomically resolved protein functions to understand how nature tamed chemistry over all conceivable length scales. This study will provide a definitive test of the collective mode coupling model (Miller Acc. Chem. Research 1994) to bridge chemistry to biology, which will be discussed as the driving force for this work.
Many-electron effects in calculated laser-induced electron diffraction spectra of laser-driven molecules

T. Tung Nguyen-Dang, François Dion

Université Laval, Département de Chimie&COPL, Québec.

Keywords: LIED, Photoelectron spectra, Many-electron effects, SAE vs Ab-initio

The recently developed [1,2] ab-initio methodology for the calculation of N-electron wavepackets in an ultrashort, intense laser pulse is used to study the dynamics of electronic excitations and ionization of CO$_2$ in an intense 800 nm laser pulse. Emphasis is placed on many-electron, many-orbital effects in channel-resolved momentum distributions of the photoelectron, in both the high-energy region corresponding to Laser-Induced Electron Diffraction (LIED [3,4]) signal, and the holographic part [5,6] of the spectra. Fringe patterns in the LIED spectrum can be shown to result from a general conservation law that of the symmetry of the initial molecular state, and a symmetry breaking analysis can be used to assess the stability of LIED readings with respect to molecular misalignment. How these ideas are brought out in the photoelectron momentum spectra obtained within the Single active electron (SAE) [3,4] and in the full N-electron calculations are discussed, highlighting many-electron, many-orbital effects in the dynamics of the laser-driven molecule.

References

Circular polarization in attosecond phenomena and applications

Andre D Bandrauk

Laboratoire de Chimie Theorique, Universite de Sherbrooke, Sherbrooke, Quebec, Canada- andre.bandrauk@usherbrooke.ca

The imaging and ultimate control of electrons in matter requires laser pulse durations on a time scale associated with the atomic unit of time- 24 attoseconds (1 as = 10^{-18}s), the time for the 1s electron in the H atom to cross the Bohr radius, a_0 = 0.0529 nm. Attosecond pulses at photon energies corresponding to the fundamental edge of matter, the soft X Ray region above 200 eV permit the probing, imaging of electronic dynamics in matter. A soft X Ray pulse duration of 43 asec has recently been achieved using intense linear polarization driving pulses [1]. The main source of current linear polarization attosecond light pulses is high order harmonic generation, HHG in atoms and MHOHG in molecules. It is a highly nonlinear nonperturbative response of electrons in matter to ultrashort, femtosecond (1 fs = 10^{-15}s) intense ( I > 10^{14} W/cm^2) mid-IR laser pulses. The highly nonlinear radiative emission is modelled now as a recollision process after tunnel ionization in linear polarization, called the Corkum model, giving a cut-off, ie, maximum photon energy at Ip +3.17 Up [2], where Ip is the ionization potential, Up = E^{2/4}w^2 at maximum field amplitude E and frequency w. Recollision is suppressed with circularly polarized pulses whereas as shown as early as 1995 multiple frequency linear polarisation pulses [3] or a combination of co- or counter-rotating bichromatic circular polarization pulses with frequencies w_1/w_2 = n_1/n_2 for integer n [4-5] induce recollision and copious harmonics of circular polarization [6-8] which are produced efficiently with counterrotating circular polarization pulses by recollision. The circular bichromatic pulse induced circular polarized HHG has been shown to be universal with a maximum intensity at photon energies Ip + 2Up and also a maximum energy cut-off Ip + 3.17Up but with Up calculated with the average frequency w = (w_1+w_2)/2. Furthermore simulations based on molecular TDSE’s (Time-Dependent Schroedinger Equations) show that circularly polarised HHG and attosecond pulses are generated efficiently when the total counter-rotating bicircular electric field rotational symmetry Cn is the same as the symmetry of a target molecule [7-8]. The compatibility of net electric field and molecular symmetries allows also to create coherent electron currents, sources of intense attosecond magnetic field pulses [8-9] for future applications in ultrafast magneto-optics [10].

References

Molecular movies from ultrafast time-resolved gas phase X-ray scattering

Peter M. Weber, 1 Michael P. Minitti, 2 Brian Stankus, 1 Jennifer Ruddock, 1 Nikola Zotev, 3 Haiwang Yong, 1 Wenpeng Du, 1 Nathan Goff, 1 Yu Chang, 1 Darren Bellshaw, 3 Mengning Liang, 2 Sebastian Boutet, 2 Adam Kirrander 3

1 Brown University, Department of Chemistry, Providence, R.I., USA – Peter_Weber@brown.edu
2 SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA
3 EaSTCHEM, School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, UK

Keywords: Ultrafast time resolved scattering, gas phase X-ray scattering

Historically, X-ray diffraction measurements have been confined to condensed phase and static systems. X-ray scattering of gaseous molecules has been a challenge due to the combination of low scattering cross-sections and low molecular densities. However, the outstanding brightness of modern X-ray Free Electron Lasers (XFELs) coupled with ultrashort pulse durations have made it possible to record movies of gas-phase chemical reactions as they unfold by recording the time-dependent X-ray scattering images after a laser pulse initiates the reaction.

While still in its infancy, the method promises to fulfill a longstanding dream by revealing nuclear motions, i.e. the motions of the atoms during a chemical reaction. Since the scattering signal derives from the total molecular wave function, the time-dependent scattering patterns carry the signatures of rotations, nuclear positions and even electron density distributions.

In our pioneering study of 1,3-cyclohexadiene [1], excitation at 267 nm results in time-resolved scattering patterns that reveal the structural evolution during the electrocyclic ring opening reaction on a 100 fs time scale. Separate photoionization measurements corroborate the dynamic time scales, and show the time evolution of the excited electronic wavepacket. Additional scattering experiments with 200 nm excitation reveal a very different picture: The excitation then leads the molecule to a 3p state with a lifetime of several hundred femtoseconds. We observe a dual decay process that includes a ring-opening reaction on a much slower time scale.

Most recently, we have shown the versatility of ultrafast gas-phase x-ray scattering by investigating a variety of model systems. In N-methyl morpholine, we observe coherent structural dynamic motions upon ionization and upon excitation to a Rydberg level. In the latter case, the coherence of the structural motions survives the electronic relaxation from the initially excited 3p to the lower 3s level, as confirmed by photoelectron measurements [2].

Acknowledgements

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References


Exploring the quantum / electron crystallography nexus

Philip Nakashima

Dept. of Materials Science & Engineering, Monash University, Victoria 3800, Australia – philip.nakashima@monash.edu

Keywords: transmission electron microscopy, quantitative convergent-beam electron diffraction, nanocomposites, metals physics, density functional theory.

Over the years, quantum crystallography has gone beyond the original definition of being a “technique for extracting quantum mechanically valid properties from X-ray diffraction experiments” [1] and now includes electron diffraction experiments as part of a suite of experimental approaches that contribute to this vibrant field [2].

Over the last three decades or so, quantitative convergent-beam electron diffraction (QCBED) has become established as an accurate technique for measuring structure factors of the crystal potential from very small volumes of material (see [3] for a review). The properties of charge and mass mean that electrons can be accelerated by electric fields to specific energies, and therefore specific wavelengths, and can also be routinely focused into sub-nanometre diameter probes (sub-Ångström in the latest generation of electron microscopes). Electromagnetic optical elements in transmission electron microscopes (TEMs) allow for very precise and accurate positioning of such electron probes in regions of interest of the specimen and the spatial selectivity is only limited by the probe size. In addition, the property of charge means that electrons interact with matter about 4 to 5 orders of magnitude more strongly than other forms of radiation used for diffraction experiments and specimens must therefore be no thicker than a few hundred nanometers. This means that QCBED can measure structure factors from volumes of material more than 10 orders of magnitude smaller in than most other types of diffraction experiments.

The relationship between electron and X-ray diffraction and the structure factors that they measure is illustrated schematically in figure 1. The easy interconversion of one type of structure factor into the other via the Mott formula [4] (based on Poisson’s equation) means that electron and X-ray diffraction can be used in complementary ways that take advantage of the strengths of each method whilst overcoming their individual disadvantages. Being able to combine these experimental methods is therefore one of the many experimental strengths within the field of quantum crystallography and represents a primary nexus of this field with that of electron crystallography. Whilst this theme is worthy of exploration in itself, the present work will look beyond this complementarity and explore areas that QCBED could open up through its ability to be spatially selective at the nanometer scale.
Fig. 1: A schematic illustration of the interaction of X-rays with the periodic electron density in a crystal, \( \rho(r) \), and electrons with the periodic crystal potential, \( V(r) \). The relationship between the electron density structure factors, \( F_g \), and those of the crystal potential, \( V_g \), is expressed by the Mott formula [4], which is derived from Poisson’s equation. A single (kinematic) scattering approximation for interpreting X-ray diffraction intensities, \( I_g \), makes them direct observables of structure factors. In the case of electron diffraction, interpretation of the diffracted intensities requires a full dynamical scattering treatment. The recorded intensities are complicated functions of not only the structure factors, \( V_g \), but also the specimen thickness, \( H \), the electron energy, \( E_0 \), and the scattering angle, \( \theta \), i.e. \( I_g = f(V_g, H, E_0, \theta) \).

Fig. 2: Testing the electron density domain theory (EDDT) [5] of precipitate nucleation and growth within alloy solid solutions using scanning, in situ QCBED. The present example schematically illustrates a hypothetical alloy in which atoms of element “a” are dissolved in a parent crystal structure having atoms of type “m”. Heat treatment (known as artificial aging) generally results in the precipitation of another crystalline phase, “p”. Invariably, a, m and p will have different electronic structures. Collecting CBED patterns across a rastered array of probe positions and mapping structure factors measured from them in different colours as the alloy is heat treated may be a way of verifying the EDDT.
Beginning with recent measurements of bonding electron density in elemental metals [3, 5, 6], the present work will move into a discussion of QCBED structure factor measurements in nanostructured materials and the potential for the technique to be able to measure vacancy concentrations and their interplay with electronic structure and lattice parameters. This will lead to discussion of a newly proposed theory for the driving force behind nucleation of secondary phases and their growth in crystalline solid solutions (alloys). The electron density domain theory (EDDT) [5] considers nucleation and growth of secondary phases within solid solutions from the point of view of domains of differing electronic structures evolving to the point where they are able to support a structural transformation leading to what is traditionally called a critical nucleus. Performing QCBED in scanning mode with a sub-nanometre electron probe while heat treating an alloy solid solution inside a TEM may be the only way to verify this theory experimentally (see figure 2).

Acknowledgements

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References

Quantum effects and properties of nanoconfined molecular rotors?

Pierre-Nicholas Roy 1

1 University of Waterloo, Department of Chemistry, Waterloo, Canada – pnroy@uwaterloo.ca

Keywords: Quantum molecular solids, endohedral fullerenes, quantum monte Carlo, Feynman path integrals

Molecular assemblies are often described using classical concepts and simulated using Newtonian dynamics or Classical Monte Carlo methods. At low temperatures, this classical description fails to capture the nature of the dynamics of molecules, and a quantum description is required in order to explain and predict the outcome of experiments. In this context, the Feynman path integral formulation of quantum mechanics is a very powerful tool that is amenable to large-scale simulations [1]. We will show how path integral simulations can be used to predict the properties of molecular rotors trapped in environments such as parahydrogen [2] and endofullerenes. We will also show that path integral simulations can be used to predict the Raman spectra of parahydrogen clusters [3] and solids. We will present ongoing work on the simulation of molecular rotors confined in endohedral fullerene materials such as H$_2$O@C60 and HF@C60 [4]. The questions we will address include symmetry breaking, spin conversion, the nature of dipole correlations and dielectric response, and entanglement measures [5-7] in assemblies such as peapods (Fig. 1) and two-dimensional solids.

![Fig. 1 Cartoon representation of an endofullerene peapod.](image)

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References

Nano cool, micro cooler! What do we want in our plasmonic materials, bandgap or no bandgap?

Vaibhav Thakore, Janika Tang, Kevin Conley, Tapio Ala-Nissila, Mikko Karttunen

1 Department of Applied Mathematics, University of Western Ontario, London, Canada – vthakore@knights.ucf.edu
2 Department of Applied Physics, Aalto University, Helsinki, Finland
3 QTF Center of Excellence, Aalto University, Helsinki, Finland
4 Department of Mathematical Sciences and Department of Physics, Loughborough University, Loughborough, UK
5 Department of Chemistry, University of Western Ontario, London, Canada

Keywords: Semiconductor plasmonics, thermoplasmonics, Mie scattering, multiscale modeling of radiative heat transfer

Plasmonically enhanced absorption or scattering of radiation on the mesoscale forms the basis of promising applications in a wide variety of fields such as: biosensing, photothermal therapy, photocatalysis, solvothermal chemistry, energy harvesting, magnetic recording for data storage, control of radiative heat transfer and so on. In a majority of the applications based on plasmonics, the noble metals - gold (Au) and silver (Ag) - have been the materials of choice. However, it is also now widely acknowledged that these materials suffer from problems of poor thermal and chemical stability accompanied by significant dissipative losses under high-temperature conditions. These issues have thus prompted a quest for materials with better thermoplasmonic properties. In this regard, semiconductor particles have lately attracted a lot of attention because they exhibit low ohmic losses, are thermochemically more stable, and exhibit highly tunable plasmonic resonances through bandgap engineering, control over dopant concentration and dielectric environment. Here, we will present results from our recent work on the multiscale modeling of plasmonically enhanced control of heat radiation using low-bandgap semiconductor microinclusions [1, 2]. Furthermore, a comparison of the size-dependent thermoplasmonic behavior of indirect and direct bandgap semiconductor particles of undoped silicon (Si) and gallium arsenide (GaAs), respectively, with the metallic (Au) particles that are characterized by a complete absence of the bandgap will also be presented [3].

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References

Joint refinements on YTiO₃: state of the art and first steps to the wave functions refinement.

Nicolas Claiser,¹ Ariste Bolivard Voufack,¹ Iurii Kibaliv,¹ Béatrice Gillon,² Yoshiaru Sakurai,³ Kunihiisa Sugimoto,³ Masahisa Ito,⁴ Claude Lecomte,¹ Mohamed Souhassou,¹ Zeyin Yan,⁵ Saber Gueddida,⁵ Jean Michel Gillet⁵

¹ CRM2, Institut Jean Barriol, Université de Lorraine and Centre National de la Recherche Scientifique, Vandoeuvre-les-Nancy, BP70239, 54506, France - nicolas.claiser@univ-lorraine.fr
² Laboratoire Léon Brillouin, CEA, Centre National de la Recherche Scientifique, CE-Saclay, 91191 Gif-sur-Yvette, France
³ JASRI/ Spring-8, Japan
⁴ Photon Factory of KEK & Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan
⁵ Laboratoire SPMS, UMR 8580, Centrale Supélec, 92295 Chatenay-Malabry, France

Keywords: insert up to five, keywords or short key phrases

The studied compound, YTiO₃, is a perovskite which presents a ferromagnetic ordering below 29K. The measured moment at saturation of 0.84μB.mol⁻¹ corresponds to a single unpaired electron located on the Ti atom [1] which is surrounded by 6 oxygen atoms. This octahedra is slightly elongated (Figure 1). A previous neutron diffraction experiment showed that the magnetic structure is complex, with a main ferromagnetic ordering component along the c-axis and two weak antiferromagnetic components along the a and b axes [2]. For a deeper understanding of the magnetic behaviors observed in the perovskite family ranking from ferro to antiferromagnetic depending on the distortion observed between octaedra, we want to explore more precisely the electronic structure of this crystal. Our project aiming to characterize the magnetic pathways using the joint refinement of X-ray, polarized neutron diffraction, magnetic X-ray diffraction and Compton scattering experiments [3].

The present work describe the charge density modeling based on a 20K diffraction data set obtained on the BL02B1 beamline at Spring8. Then, a data set measured thru magnetic X-ray diffraction realized at KEK and a set of flipping ratios measured by polarized neutron diffraction on beamline 5C1 at LLB in Saclay were added to achieve a jointly refined model (Figure 2). This common model will be described in the presentation as well as the difficulties to obtain it.
Fig. 2 Static electron density in different planes: Ti-O2-O2', Ti-O1-O2', Ti-O1-O2 respectively. NLOG weighting scheme, contours at 0.05 eÅ$^{-3}$, blue: positives, red: negatives.

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References

Donor-acceptor stabilization of, and bonding in, low-oxidation state main group element hydrides

Alex Brown,¹ Evan Antoniuk,¹ Eric Rivard¹

¹ University of Alberta, Department of Chemistry, Edmonton, AB, T6G 2G2 Canada – alex.brown@ualberta.ca

Keywords: Group 14 hydrides, Frustrated Lewis pairs, Density functional theory, Bonding analysis, Energy decomposition analysis

Recently, much synthetic effort has been placed in attempting to prepare low oxidation state main group hydrides. Primarily, this has been accomplished by using a combination of N-heterocyclic carbenes (electron donors) and Lewis acids (electron acceptors) to stabilize these reactive hydrides. In this talk, the structures, stability, and nature of bonding for Group 14 element dihydrides (Si, Ge, Sn, and Pb) when trapped by an intramolecular frustrated Lewis pair ligand have been studied computationally using density functional theory (M06-2X/cc-pVTZ), DLPNO-CCSD(T) single point computations, energy decomposition analysis (EDA) Natural Bond Orbital (NBO) analysis, and the Quantum Theory of Atoms-in-Molecules (QTAIM). The bonding will be compared to the known donor-acceptor stabilized complexes involving SiH₂, GeH₂, and SnH₂ [1-5]. The computational results suggest the compounds (except for Pb dihydride) can be prepared experimentally under mild reaction conditions.

Acknowledgements

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References

Novel nanocrystalline material and their application

Khashayar Ghandi\textsuperscript{1,2}

\textsuperscript{1} University of Guelph, Department of Chemistry, Guelph, Ontario, Canada – kghandi@triumf.ca
\textsuperscript{2} Laboratoire de Chimie Physique, Université Paris Sud, 15, avenue Jean Perrin 91405 Orsay, France

**Keywords:** Nanostructures, Magnetic field, Gravity, Biosensors, Radiation

Research on metal and metal oxide nanomaterials has been active because of the extensive diversity of applications that sometimes need a good control of their morphologies and their surface. Although, nanocrystals have been studied for decades it is only recently that we see their applications in technology. New developments in our group to make nanocrystalline material as well as their applications will be discussed in this presentation. At first, use of two weak fields that due to their weak interactions they have not been explored much in chemical approaches for synthesis of crystalline material based on non-magnetic molecules will be discussed. The two field are gravity and magnetic fields. Then novel applications and properties of the nanocrystals that have been made in our labs will be discussed. The fundamental and applied aspects will helpfully convince theoretical and computational chemists to study them so that we, together (experimental and computational/ theoretical chemists), can develop ground breaking applications.
On the control parameters of pressure-induced bond activation/compression

Wolfgang Scherer,¹ Dominik Schmitz,¹ Marcel Vöst,¹ Marcel Kalter,¹ Georg Eickerling¹

¹ Institute of Physics, University of Augsburg, Augsburg, Germany, Email: wolfgang.scherer@physik.uni-augsburg.de

Keywords: extreme conditions, high pressure, bond activation, bond compressibility

In general it is assumed that “forces in crystals act through localized bonds” which in turn can be identified by the presence of a bond path.[1] In case of highly symmetrical covalent compounds, hardness has been originally defined by the bulk modulus \( B \) and is controlled by the compressibility of their individual chemical bonds [1]. These earlier case studies showed that the bond compressibility usually increases with enhancement of the bond ionicity and by lowering of the bond strength [2]. In case of molecular crystals, however, the scenario is more complex and the low bulk modulus is often reflecting the softness of van der Waals contacts at lower pressure [1]. Furthermore, chemical bond activation might be enhanced under external pressure and might result in a negative bond compressibility. In the following we will outline criteria based on the topology of the scalar fields of the negative Laplacian, \( L(r) = -\nabla^2 \rho(r) \), and the Electron Localization Function, \( \eta(r) \), which control pressure-induced bond activation or compression mechanisms in organometallic compounds displaying \( M\text{-C}, C\text{-H} \) and Si-H bonds. In case of the isostructural Group IV metallocene complexes \( L_2\text{TiMe}_2 \) (\( M = \text{Ti, Zr, Hf}; \ L_2\text{Ti} = \text{ansa-bidged titanocene fragment} \)) we outline how ligand-induced charge concentrations in the valence shell of the metal control the positive bond compressibility of \( M\text{-C} \) bonds (Figure 1) [3]. In contrast, the influence of valence charge depletion zones on the negative bond compressibility of activated Si-H and C-H bonds is demonstrated in case of \( \sigma\)-silane and alkane complexes [4,5].

Fig. 1 ELF (\( \eta(r) \)) and negative Laplacian (\( L(r) \)) contour map in the TiMe₂ plane of the metallocene \( L_2\text{TiMe}_2 \).

References


Atomic and molecular properties of diatomic molecules in external electric fields

Shahin Sowlati-Hashjin,1 Chérif F. Matta2

1 Dept. of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 3K7. shishjin@uwo.ca
2 Dept. of Chemistry and Physics, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2J6. cherif.matta@msvu.ca

Keywords: Molecules in strong fields, QTAIM properties, Diatomic molecules

It has been previously shown that response properties (changes in total energies and in equilibrium bond lengths, and vibrational Stark shifts) of nine diatomics in external uniform electric fields (EFs) of strength up to $10^{10}$ V/m in directions parallel and antiparallel to the permanent molecular dipole moment (for dipolar molecules) can be predicted from field-free values using a simple model of a field-perturbed Morse potential [1]. The molecular set ($\text{H}_2$, $\text{N}_2$, $\text{O}_2$, $\text{F}_2$, $\text{Cl}_2$, $\text{HF}$, $\text{HCl}$, $\text{CO}$, $\text{NO}$) has been chosen to include non-polar and polar diatomics with average polarizability ranging from low to high [1].

The present work investigates the correlation between EFs and quantum theory of atoms in molecules (QTAIM) atomic and bond properties such as localization and delocalization indices (LIs and DIs), atomic charges ($q(\Omega)$), and electron densities at bond critical points ($\rho_{\text{BCP}}$) [2].

![Fig. 1](image)

**Fig. 1** The change in the delocalization index, $\Delta \delta(\Omega,\Omega')$, as a function of the electric field strength ($E$) in V.m$^{-1}$ for the homo-nuclear diatomics (left) and of the field strength and direction for the hetero-nuclear diatomics (right). ($\Delta \delta(\Omega,\Omega') = \delta(\Omega,\Omega')_{E} - \delta(\Omega,\Omega')_{0}$, where the subscripts $E$ and 0 refer to the presence and absence of external field, respectively).

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References


Bonding formation along the pressure-induced B3-B1 phase transition in InP

J. M. Recio,1 H. H. Osman,1,2 J. Andrés,2 M. A. Salvadó1

1 MALTA-Consolider Team and University of Oviedo, Oviedo, Spain – jmrecio@uniovi.es
2 MALTA-Consolider Team and University Jaume I, Castellón, Spain – andres@qfa.uji.es

Keywords: Chemical Pressure, Chemical Bonding, Phase Transition, High Pressure

Using the real space resolution of the electronic energy derived from density functional theory (DFT) electronic structure calculations, a so-called chemical pressure (CP) can be evaluated [1]. The raw data for the generation of maps displaying how this CP evolves along the unit cell of a crystalline solid is obtained through three single-point crystal energy calculations spanning a volume range of 3% around the equilibrium geometry. These quantum mechanical calculations were performed within the LDA exchange-correlation approximation using HGH atomic pseudopotentials by means of the ABINIT package [2,3]. Recently, this DFT-CP formalism has been proposed to study the chemical bond nature in a wide variety of molecules and materials [4]. In this contribution, we illustrate the capability of the new approach to clearly track the formation of chemical bonds using the crystal of Indium Phosphide as a target system. InP undergoes a pressure-induced phase transition with a net increasing of the atomic coordination number from 4 in the zinc blende to 6 in the rock-salt phase [5]. An orthorhombic unit cell of Imm2 symmetry allows us describing the transition path. The identification of a signature detecting the formation of new bonds is accomplished by searching for the appearance of absolute minima of negative CP along interatomic lines. We show that the emergence of two new In-P bonds is unequivocally detected in the chemical pressure maps once the activation barrier of the transition path is overcome (see Fig.1).

Fig. 1 3D chemical pressure maps showing black isosurfaces of CP = -0.052 a.u. in the orthorhombic unit cell of InP (In = blue, P = purple) at selected values of the transformation coordinate ξ along the transformation path.
Acknowledgements


References

Pentacoordinated silicon compounds as a model system to study S\textsubscript{N}2 reactions

Malte Fugel,\textsuperscript{1} Maksym V. Ponomarenko,\textsuperscript{1} Simon Grabowsky\textsuperscript{1}

\textsuperscript{1} Institute of Inorganic Chemistry and Crystallography, University of Bremen, Bremen, Germany – m.fugel@uni-bremen.de

Keywords: Complementary bonding analysis, X-ray wavefunction refinement, S\textsubscript{N}2 reactions

Nucleophilic substitutions of S\textsubscript{N}2 type are indubitably among the most common and important reaction mechanisms. For that reason, a large number of studies investigating the reaction pathway of S\textsubscript{N}2 reactions at carbon and silicon centers can be found in the literature.\textsuperscript{[1]} In most of these studies, the approach of the nucleophile towards the electrophilic center has been modeled based on quantum chemical calculations, since methods to capture a “molecular movie” are only just emerging through the recent development of free electron lasers and intense electron beams.\textsuperscript{[2]}

Fig. 1 The framework of the pentacoordinated silicon compounds and a list of the substituents X.

In the present study, an intramolecular S\textsubscript{N}2 reaction at a silicon center is investigated based on the idea of Bürgi's structure correlation, which makes an experimental investigation of a pseudo-reaction pathway feasible.\textsuperscript{[3]} Pentacoordinated silicon compounds are the ideal model system used for that purpose in the past.\textsuperscript{[4]} Our system consists of the peri-substituted naphthalene framework shown in Figure 1, and a systematic array was synthesized where the substituent X, which simulates a leaving group, is varied among the different compounds. The interaction between the nucleophilic nitrogen and electrophilic silicon (frustrated Lewis pair) is enhanced by an increase in the leaving group ability of X, and, thus, it is possible to tune the strength of the N-Si interaction with the choice of X. Consequently, the crystal structures of the pentacoordinated silicon compounds can be regarded as snapshots of a pseudo S\textsubscript{N}2 reaction pathway, with weak leaving groups representing early steps, strong leaving groups more advanced steps, and the silyl cation the end product of the S\textsubscript{N}2 reaction.

In an advancement of the structure-correlation concept, we go beyond pure geometry in that we investigate the correlation of electronic bonding properties along the pseudo-reaction pathway. We performed X-ray wavefunction refinements (XWR) \textsuperscript{[5]} based on high resolution, low temperature synchrotron X-ray diffraction data of the respective crystal structures measured at SPring-8. Geometry optimizations were performed to complement the results from XWR. Based on these experimentally fitted and theoretical wavefunctions, a complementary bonding analysis,\textsuperscript{[6]} which entails bonding descriptors from both real space (QTAIM \textsuperscript{[7]} and ELI-D \textsuperscript{[8]}) and orbital space (NBO \textsuperscript{[9]}), was carried out.
It has been possible to find a variety of correlations with respect to bonding and geometrical properties of the N-Si interaction and Si-X bond. Figure 2 shows two of these correlations: a) The electron density and the total energy density at the Si-N bond critical point across all different compounds and b) the total energy density at the Si-X bond critical point plotted against the N-Si distance.

Fig. 2 a) The electron density and the total energy density at the Si-N bond critical point ($\rho_{bcp}(N-Si)$ and $H_{bcp}(N-Si)$) and b) the total energy density at the Si-X bond critical point ($H_{bcp}(Si-X)$) plotted against the N-Si distance.

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We thank many collaboration partners who have contributed significantly to this study. We will mention all of them by name in the talk.

References

The Miguel A. Blanco Prize Lecture:

The pair density as a source of chemical information

Eduard Matito\textsuperscript{1, 2}

\textsuperscript{1} Donostia International Physics Center (DIPC), Donostia, Spain – ematito@gmail.com
\textsuperscript{2} Ikerbasque Science Foundation, Bilbao, Spain.

Keywords: pair density, electron delocalization, local spin, electronic localization function, multicenter bonding

The pair density is a key quantity in quantum chemistry that provides, among others, the expected value of the total potential energy. Following Born's interpretation of the wave function \cite{1}, it can be related to the probability of finding a pair of electrons at two points of the Cartesian space. This quantity has been used to construct well-known quantities in the chemical bonding community such as the electron localization function \cite{2}, the delocalization index \cite{3-5} or the local spin \cite{6-7}. In this talk, we review this concept and some of the quantities that are based on the pair density at the time we provide some recent examples of how to extract chemical information from this function. These chemical bonding tools are also shown to provide stringent conditions on the quality of the pair density that can be used to assess approximate pair densities \cite{8-10}.

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Quantum Chemical Topology (QCT) [1-3] is a parameter-free methodology that uses the concept of a gradient path to extract chemical information from a quantum chemical density function. QCT’s topological energy partitioning[4], currently called Interacting Quantum Atoms (IQA) [5], defines amongst other energy contributions the intra-atomic energy [6], which is a classical interatomic repulsion energy (see the Buckingham potential), and the interatomic exchange energy $V_x(A,B)$. From this quantity one can draw [7] the Lewis diagram of any molecular system, and classify interactions by their degree of covalency. Hence the term non-covalent interaction is too blunt. Anomalously large values of $V_x(A,B)$ compared with interatomic distance point at remarkable interactions[8].

For the first time, we combined [9, 10] IQA with MPn ($n=2,3$ or 4), and found that in terms of van der Waals dispersion, the correlation energies represent an atomic stabilisation, by proximity to other atoms, as opposed to direct interactions with other nearby atoms. More recent work [11] shows that electron correlation lowers the energy of the atoms at either end of a bond, but for the bond itself, it can be stabilizing or destabilizing by the inclusion of the excited states incorporated through MPn. We show a key diagram (Figure 1) that explains why ionicity is not the opposite of covalence although one may have been taught so. Finally a study [12] on small water clusters shows that electron correlation energies are transferable within 3 kJmol⁻¹ (Figure 2).

**Figure 1.** Charge Transfer against absolute values of (a) bond correlation and (b) bond exchange. Negative values for bond correlation are marked in purple. Note that charge transfer is defined to be always positive.
References


Electron counting in position space: From quantum fragments to Lewis structures to multicenter bonds

Ángel Martín Pendás,¹ Evelio Francisco²

¹Universidad de Oviedo, Departamento de Química Física y Analítica, Oviedo, Spain – ampendas@uniovi.es
²Universidad de Oviedo, Departamento de Química Física y Analítica, Oviedo, Spain – evelio@uniovi.es

Keywords: Quantum Chemical Topology, Electron Counting, Atoms in Molecules, Multicenter bonds.

An electron counting technique to generate Lewis structures from position space partitioning procedures is proposed. We base our approach on reformulating the adaptive natural density partitioning (AdNDP) algorithm proposed by Zurek and Boldyrev [1] real space through the use of domain-averaged cumulant densities, which take into account many electron correlations. Averages are performed over the basins provided by the quantum theory of atoms in molecules. The decomposition gives rise to a set of n-center, two-electron orbitals which describe the dominating Lewis structures of a molecular system, and is available both for single- and multi-determinant wavefunctions.

As shown in several examples [2], chemically intuitive descriptions, in close correspondence to those obtained through the AdNDP recipe, are now available from fully orbital invariant position space descriptors.

References

Density meets orbitals [1]

Lukas Bucinsky

Slovak University of Technology, Department of Chemical Physics, Bratislava, Slovakia – lukas.bucinsky@stuba.sk

Keywords: Quantum Crystallography, DFT, CASCCF, orbital, density

Herein we will turn our attention to the exploration of electronic structure from the perspective of orbitals. To prevent a complicated interpretation in the orthonormal canonical Hartree-Fock (HF) and/or Kohn-Sham (KS) orbitals picture, we will stick to the Complete Active Space (CAS) natural orbitals and extend these to the analysis of d-populations and localized orbitals under KS description. Nevertheless, we will put emphasis also on the comparison of the above mentioned results to the KS electron density topology from QTAIM analysis [2]. We will compare density and orbitals to see the resonance and differences in the interpretation of the density and orbital pictures, albeit sticking merely to the one-electron density approximation.

We will choose systems which turned out to be interesting from the perspective of having a different magnetic state preference [3], having a different electron configuration at HF and KS and/or CAS levels of theory [4], or from the perspective of their magnetic behavior (the sign of the \( D \) parameter in zero field splitting) which is governed by the geometry [5], i.e. X-ray structure vs. optimized geometry.

From the perspective of quantum crystallography [6], we will explore the neutron diffraction results contra theoretical DFT and CAS calculations [4]. Similarly, we will put under spotlight the multipolar refinement in transition metal complexes to point out the found differences and similarities with respect to DFT based electron density topology, QTAIM and d-populations [7].

Acknowledgements

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References

X-ray charge density study of chemical bonding in ZnSb

Hidetaka Kasai,1 Jiawei Zhang,2 Kasper Tolborg,2 Anders B. Blichfeld,3 Mattia Sist,2 Venkatesha R. Hathwar,1 Jacob Overgaard,2 Eiji Nishibori,1 Bo B. Iversen2

1 Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba, Japan – kasai.hidetaka.fw@u.tsukuba.ac.jp, nishibori.eiji.ga@u.tsukuba.ac.jp
2 Center for Materials Crystallography (CMC), Department of Chemistry and iNANO, Aarhus University, Denmark – bo@chem.au.dk
3 Department of Materials Science and Engineering, Norwegian University of Science and Technology, Norway

Keywords: Electron charge density, Synchrotron X-ray diffraction, Zinc antimonide

ZnSb is a thermoelectric material with low thermal conductivity. Madsen and coworkers found the Sb-Sb dumbbell rattling model is unlikely due to contribution of both Zn and Sb vibrations to low-energy optical modes [1]. The low thermal conductivity could originate from its chemical bonding [2]. ZnSb is an electron-poor II-V semiconductor with 3.5 valence electrons per atom, which is less than 4 valence electrons per atom in tetrahedrally bonded semiconductors. Since the charge transfer calculated from theoretical charge density is only ±0.27, chemical bonding in ZnSb is covalent rather than ionic [3,4]. The structure of ZnSb consists of planar rhomboid Zn2Sb2 ring which are connected to the other rings by Zn-Sb or Sb-Sb. Each atom has a fivefold coordination and topological analysis of the theoretical charge density shows these are bonding interactions [2]. It has been considered that the Zn2Sb2 ring built by 4 center 4 electron (4c4e) bonding is connecting by 2 center 2 electron (2c2e) bonds [4,5]. This bonding picture has been discussed based on the theoretical charge density. It is important to understand the peculiar chemical bonding in ZnSb, which is related to physical properties.

Accurate X-ray charge density enables observation of not only strong covalent but also weak interactions [6,7], which are decisive for properties. We conducted experimental charge density study of ZnSb. Single-crystal X-ray diffraction data were measured at 20 K with 50 keV X-ray using an image plate detector at SPring-8 BL02B1. The charge density was determined from the diffraction data with a resolution sinθ/λ < 1.67 Å⁻¹ using Hansen-Coppeens multipole model. The bonding interactions were evaluated quantitatively based on the obtained charge density by Bader's topological analysis. The experimental charge density and topological measures were compared with those obtained from density functional theory. In the presentation, we will discuss the data, charge density and chemical bonding in ZnSb.

Acknowledgements

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Electron density and real structure of materials

Yuri Grin

Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany – grin@cpfs.mpg.de

Keywords: intermetallic compound, electron density, real structure, chemical bonding, real space analysis

Intermetallic compounds are a family of inorganic substances formed by elements located left from the Zintl line in the Periodic Table. A general feature of these materials is a reduced number of electrons per atom. This is the reason, that intermetallic compounds do not follow the normal valence rules and reveal crystal structures which differ from the ‘classical’ inorganic materials. A better understanding of the crystal structure and chemical composition is necessary for interpretation of their chemical and physical properties including catalytic, thermoelectric, heavy-fermion behavior, etc.) [1].

Caused by specific bonding features – a sometimes complex interplay of ionic, polar and nonpolar covalent, two- and multi-center interactions – the crystal structures of intermetallic phases reveal local deviations from the ideal atomic arrangements as described by symmetry in the three-dimensional space. The traces of such behavior can be detected from the residual electron density by precise crystal structure determination. For the interpretation of the so-obtained density distributions, application of spectroscopic techniques, transmission electron microscopy tools and quantum mechanical studies are necessary, often in combination with each other.

In the crystal structures of CeIn$_5$Ir and CeIn$_5$Co, the presence or absence of polar covalent interactions between Ce and transition metal result in a coexistence of two different structural patterns within one single crystal (Figure 1). The majority motif (ca 98 % and more) has slightly lower energy, the minority one has weaker Coulomb contribution to the total energy. The presence of both detected in the structure determination from diffraction data is confirmed by the low-temperature STM experiments [2].

Boron carbide is one of the best studied ceramic materials. Despite that, a coherent description of its crystal structure and physical properties is still under discussion. By combining precise crystal structure determination from diffraction experiments and state of the art high-resolution transmission-electron microscopy with ab-initio computational analysis the hitherto unknown local structure alterations were found. The interplay of different local atomic arrangements reduces the electron deficiency of the real crystal structure in respect to pristine structural motif described as CBC+B$_{12}$. This allows to discuss the issue about electron precise character of boron carbide. Introducing new electronic states within the band gap allows a better description of electronic transport properties [3].

In the cage structure of clathrate-I Ba$_8$Ge$_{46-x}$Au$_x$, a detailed X-ray diffraction investigation reveals that Ba atoms in the cages are off-centered and do not fully occupy the high symmetry position, Au atoms substitute Ge atoms only partially and are off-centered. High-end transmission-electron microscopy and STEM images on the same crystal confirmed clearly those results, resulting in deviations from the translational symmetry with a wide spectrum of characteristic distances. The disorder has been studied by ab initio DFT simulations and inelastic neutron scattering [4].
Fig. 1 Coexistence of two structural patterns in the real crystal structure of CeIn$_5$Ir [2].

References

Electron density from strong-correlation wave functions

Markus Reiher

ETH Zurich, Lab. f. Phys. Chem., Zurich, Switzerland – markus.reiher@phys.chem.ethz.ch

Keywords: electron density, multi-configurational approaches, quantum chemistry

In this talk, I will discuss some of our recent work on multi-configurational wave-function methods based on the density matrix renormalization group (DMRG). The DMRG algorithm allows one to carry out complete-active-space-(CAS)-type calculations. Whereas traditional CAS approaches are limited to about 20 active orbitals, which severely restricts their applicability for strongly correlated molecular systems and molecular crystals (e.g., those built from 3d metal complexes with noninnocent ligands or from multi-nuclear clusters of 3d elements), DMRG makes up to about 100 active orbitals accessible. DMRG is therefore the best choice for strongly correlated systems for which density functional theory (DFT) usually suffers from severe limitations of the approximate density functionals. However, DMRG calculations have been reserved for expert use so far and we have made an attempt to turn them into black-box calculations that are as easy to carry out as DFT calculations. For this, we had to develop a scheme that allows one to choose active orbitals for the CAS in a fully automated manner [1-3], for which we developed a software that can carry out all steps of a DMRG calculation by pushing a single button [4]. The applicability of the approach is discussed at the example of electron-density calculations for transition metal complexes [5-7].

References

How do density functional approximations affect our results?

Julia Contreras-García, 1 Francesca Peccati, 1 Rubén Laplaza 1

1 Laboratoire de Chimie Théorique, CNRS-Sorbonne Université Paris, France
contrera@lct.jussieu.fr, francesca.peccati@gmail.com, laplazasolanas@gmail.com

Keywords: error estimation, ELF, DFT, electron density

Electron density is a quantum observable through X-rays, however, the mutual interaction of experiment and theory in Quantum Crystallography needs to understand what errors derive from the theoretical models used both in the direct calculation of solids and even in the refinement of constrained wavefunctions coupled to HF or KS schemes.

We will look at two different axes of the same question: “how does the density function approximation (DFA) chosen affect the description of a solid”?

Firstly, we will dwell on the effects of the functional on the calculated properties of a system, such as the cell geometry or transition pressures. We will aim at providing insight into how trustworthy a DFT simulation is and how important is the input from the simulator (i.e. the parameters the computational chemist can tune) [1].

Secondly, and focusing both on DFT development and constrained wavefunctions, we will try to see how the functionals chosen can affect the electron density we obtain. It has been shown that the quest for highly accurate functionals has led to big errors in the electron density [2]. But these errors have been looked at as overall errors (NRMSD), i.e. one number for a given system. However, not all parts are equally relevant for understanding the chemistry of a system: systematic errors in the core are not relevant for chemical transformations, whereas random errors in the valence can lead to unpredictable results. As an example, Figure 1 shows the Localized Orbital Locator (LOL) for CO from a set of DFAs with similar RMSD. As can be seen, very different real space errors are at the base of their failure. Whereas some of them are localized in chemical regions (lone pairs, bond), some others seem more chaotic and their effect is more difficult to predict [3].

We will address these two questions based on basic electron localization principles (delocalization error, chemical regions in terms of LOL). Although results are still preliminary in many cases, important trends appear both in the prediction of calculated error bars and the chemical source of errors in DFT descriptions by functionals families that should be useful in the understanding of the effect of density functional approximations in our calculations and refinements.
Fig. 1 Errors in the electron density of $N_2 (\rho - \rho_{\text{CCSD}})$ calculations for several functionals with similar integrated errors.

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The topological structure of complex molecules: Challenges and near future directions

Hugo J. Bohórquez

1 FIDIC, Biomathematics, Bogotá, Colombia – hugo.j.bohorquez@fidic.org.co

Keywords: electron density, topology, proteins, atoms in molecules, quantum molecular dynamics

The electron density is the central quantity in both DFT and Bader's theory of atoms in molecules (AIM) because it solely determines all the system properties. Just recently large molecular systems have been solved at good theoretical level.[1] It has been possible thanks to the implementation of fragmentation methods — some of which are close to linear scaling — that dramatically reduces the required CPU time.[2] Indeed, a PC cluster can compute the wave function of a protein in record time. In addition, grid-based studies of electron densities provide the topology of large molecules.[3,4] Now, however, the challenge is processing, analyzing, and understanding all the data from the critical points in a clear and efficient way. In this talk, I will show a pack of tools that facilitate the topological study of electronic regions in large molecular systems. In particular, the topology of the electron density can be translated into a quantum molecular structure representation that allows one to inspect the intensity and directionality of non-covalent interactions.[5] In this way, a typical AIM topological file can be visualized as a new type of quantum structure representation (QSR).[6] Thanks to a Python program written by the author it is possible to plot the QSR structure within the UCSF Chimera package simultaneously to other volumetric information such as the electron density, for instance. QSR helps avoiding ambiguities related with the interpretation of critical points in large systems, such as, e.g., noble gas atoms trapped inside fullerenes.[7]

I will show several organic systems were this tool is useful. For instance, for unveiling higher order non-covalent interactions responsible the secondary structure of peptides.[8] In addition, a poly-glicine peptide in different conformations reveals their cooperative stabilization upon backbone conformational changes. In addition, the fully-optimized protein-peptide complex at MP2 level reveals the non-covalent contacts that characterize the peptide binding region of the major histocompatibility complex class II (PDB 1HLA). I will explain why it is required the quantum mechanical optimization of proteins prior to their topological analysis. Finally, I will show the breaking and formation of chemical bonds during a quantum dynamical simulation of a chemical reaction assisted by water molecules that can be traced in time with the QSR molecular model.

Fig. 1 The quantum structure representation (QSR) of a He atom confined inside the Buckminsterfullerene; this molecular graph avoids any ambiguity regarding the presence of “bond critical points” between the helium and the sixty carbon atoms because the electron density at the critical point gauges the thickness of the bond paths. The level of theory was B3LYP/6-31G, from GAMESS and the topology was obtained with AIMAll (Version 17.11.14), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2017 (aim.tkgristmill.com). Molecular graphics were performed with the UCSF Chimera package. Chimera is developed by the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco (supported by NIGMS P41-GM103311).
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References

Comprehensive electron density analysis of 1 to 3D systems fully integrated in the ab initio CRYSTAL code

Silvia Casassa,1 C. Gatti,2 C.M. Zicovich-Wilson, M. Causà,3 P. Ugliengo1

1 University of Turin, Department of Chemistry, Turin, Italy – silvia.casassa@unito.it
2 University Department, CNR ISTM, Milan, Italy – carlo.gatti@istm.cnr.it
3 University of Naples, Department of Chemistry Ingeneering, Naples, Italy – mauro.causa@unina.it

Keywords: electron density, Bader analysis, ELF, MPD, Hirshfeld, CRYSTAL code

Through the \textit{ab initio} quantum-chemical (QM) solution of the Schrödinger equation of the ground-state of a system much attention is commonly devoted to the total energy and its derivatives as they allow to determine a variety of properties. Nonetheless, as pointed out in the emerging field of Quantum Crystallography [1], a wealth of chemical information on the system can be extracted from the analysis of its wave-function. In particular, the one-electron density matrix, which can be easily derived from it, allows to effectively compute any one-electron property of the system as electron charge density (ECD) $\rho(r)$, X-ray structure factors, electrostatic potential, Compton profile, etc.

Among the others, ECD is by far the most studied as it embodies rich information on the structure and chemical nature of the bonding framework of any systems.

In particular, several scheme have been proposed in the last decades to analyze and extract from $\rho(r)$ as much information as possible [2].

In this respect, in the CRYSTAL code [3] has been recently made available a suite of options to explore ECD properties through different complementary techniques:

(i) a complete topological analysis according to Bader [4], providing $\rho(r)$ critical points, its Laplacian and derivatives and atomic integrated properties as charge, volume and energy [5];

(ii) electron localization function [6] (ELF) as discussed and implemented in the pioneering work of Silvi and Savin [7] and the related maximum probability domain (MPD) [8];

(iii) the Hirshfeld-I partition scheme [9] generalized for open-shell crystalline systems [10].

Some of these methods were already present in previous releases of the code but now all the features are fully integrated and efficiently parallelized [11].

Few applications will be presented to show (i) the accuracy that can be reached in detecting and characterizing thin effects even in very large systems (i.e. localization of interaction sites of water with crambin) as well as (ii) the possibility to enlighten unexpected features related to ECD (i.e. quantify the strength of hydrogen-bond occurring on hydroxilated surfaces [12]).
Fig. 1 Graphical representation of the crystal structure of a) the crambin protein (1284 atoms in the unit cell) and (b) the pyrope silica garnet. ECD of both systems has been extensively studied with the parallel version of the CRYSTAL code.

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References

Next generation QTAIM

Samantha Jenkins,¹ Steven R. Kirk,¹ Tianlv Xu,¹ Michael Filatov,¹,² and Sergei Manzhos³

¹ Hunan Normal University, College of Chemistry and Chemical Engineering, Changsha, China – samanthajsuman@gmail.com
² Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea – mike.filatov@gmail.com
³ National University of Singapore, Department of Mechanical Engineering, Singapore, – sergei.manzhos@gmail.com

Keywords: QTAIM, stress tensor, photo-chemistry, molecular rotary motor, azophenine switch

QTAIM and the stress tensor theory have recently been developed to include a broad range of chemical and physical environments that including:

- New interpretation of the Ramachandran plot applicable to peptides and molecular motors [1].
- The normal modes of vibration of benzene in a stress tensor space [2].
- The dynamics of fast and slow trajectories of a light-driven rotary molecular motor explained by sticky bonding interactions [3].
- Understanding fatigue and photochromism of the S₁ excited state of diarylethenes [4].
- The functioning of doped azophenine switches in a stress tensor space.
- Distinguishing and quantifying the torquoselectivity in competitive ring-opening reactions [5].
- Isomerization of the RPSB chromophore in the gas phase along the torsional pathways using QTAIM [6].
- Investigation of stereochemistry to show anisotropy from QTAIM eigenvectors.
- Demonstrated standard treatments of relativistic effects insufficient for the [Sb₃Au₃Sb₃]³⁻ complex [7].
- A new vector based interpretation of the chemical bond [8], see Fig 1.

![Fig 1](image)

**Fig 1.** The light-blue and red line shown represent the paths swept out by the tips of the scaled $e₁$ and $e₂$ eigenvectors corresponding to the eigenvector-following path lengths $H^*$ and $H$ are shown schematically in (a) and (b) respectively. The arrows representing the $e₁$ and $e₂$ eigenvectors, scaled by the ellipticity $ε$, where the vertical scales are exaggerated for visualization purposes. The green sphere indicates the bond critical point. The bond-path framework set B comprises the paths $p$, $q$ and $r$, of lengths $H^*$, $H$ and the bond-path length (C2-C3) defined by $e₃$. Actual results for formic acid are presented in (c).
Acknowledgements

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References

The electron density at the complete basis set limit

Seyed Abdolreza Sadjadi

The University of Hong Kong, Faculty of Science, Laboratory for Space Research, Hong Kong (SAR), China – ssadjadi@hku.hk

Keywords: Electron Density, QTAIM, CBS limit, Convergence Pattern, Error Free Topological Properties

The complete basis set limit is one of the most important points in the wavefunction (many electron approximations)-basis sets (one electron approximation) combination space within the Born-Oppenheimer time independent framework of Schrödinger equation. It is a unique point in which the mathematical errors due to these two main approximations in quantum chemistry models, are well separated and thus evaluable.

The pioneering works of Dunning, Feller, and Peterson [1-6] has made this critical theoretical point, reachable in a systematic way. This has been done through the extensive calculations of molecular energies and all other potential energy surface-dependent properties. The impact of such an approach for accurate calculations of various molecular spectroscopic and thermodynamic properties has been well established and documented [4-6].

In this respect, it is straightforward to ask what would happen to the electron density and its dependent properties when the calculations are approaching the complete basis set limit?. Part of the answer to this fundamental question has been provided in a recent publication on the study of the electron density of the \( \text{H}_3^+ \) (Figure 1) [7].

In this talk, this fundamental question will be addressed by discussing the results of fine-tuned calculations on different molecular systems. The advantages of following this approach and its impact on other QTAIM based approaches [8-12] are also anticipated.

Fig. 1 The trend of convergence of total molecular energy (left panel) and electron density value at BCP point (right panel) toward CBS limit in \( \text{H}_3^+ \) at RHF/cc-pVXZ (X= D, T, Q, 5, 6). (From ref [5])
Acknowledgments

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References

Enzymatic reaction modelling as a stretch-test of machine learning based on small-molecule electron density topological training data

Preston J. MacDougall, 1 Kiran K. Donthula 1

1 Middle Tennessee State University, Department of Chemistry, Murfreesboro, USA - pmacdougall@mtsu.edu
2 Middle Tennessee State University, Department of Chemistry, Murfreesboro, USA

Keywords: Laplacian topology, machine learning, picotechnology, QTAIM, quantum atomics

Bader’s Quantum Theory of Atoms In Molecules (QTAIM) allows for the definition of well-defined, measurable, reproducible, and often transferable properties of atoms in molecules [1]. Such data can be classified as quantum atomics, and is analogous to other –omics such as genomics, proteomics, etc… We will focus on picoscale subatomic features that are well-defined (by the topological properties of the Laplacian of the electronic charge density), measurable, reproducible, and often transferable [2]. Such data is continuously being generated by multiple experimental and computational research groups worldwide, for atoms from most regions of the periodic table.

Our initial studies focus on subatomic data for the carbonyl group in over 200 compounds (amides, ketones, aldehydes). As a proof-of-principle exercise, artificial neural network (ANN) machine learning algorithms were utilized to correlate quantum atomic data to chemical properties of these compounds, including C=O stretching frequencies, C13 NMR shifts, and intermolecular interaction energies [3]. The descriptors used here are limited to calculated topological critical point properties in the measurable total charge density and its Laplacian. As a stretch-test, we investigate whether so-trained ANNs can also predict interaction energies for carbonyl groups of molecules bound to models of enzyme active sites. Our ultimate goal is that such machine learning will help develop picotechnology that will allow engineering of chemical systems that take advantage of reactive properties of atoms in molecules.

For the stretch-test we chose the  E. coli enzyme D-fructose-6-phosphate aldolase (fsa gene), which catalyzes a nucleophilic addition reaction. Aldolases typically catalyze the stereoselective addition of a carbon nucleophile (ketone) to a carbonyl electrophile (aldehyde). 3-hydroxypropanal was used as the test substrate and the fluoride ion was the nucleophile. Ab initio calculations of interaction energies of these reactions within the binding pocket of an enzyme is computationally very demanding. Reasonably accurate models that are based on the experimentally measurable electron density offer an alternative approach.

Within the context of QTAIM, the charge density topology determines molecular structure and the characterization of chemical bonds, whereas the topology of its Laplacian is related to models of electronic structure and chemical reactivity. A second over-arching goal of the study is to use both combined and separate sets of machine learning training data to differentiate the information content of these two types of topological data with respect to modeling interactions that result in covalent bonds as well as van der Waals interactions.
References

The catalytic role of hydrogen bond interactions

Aurora Costales,1 M. Gallegos,1 S. Gil-Guerrero,2 J. Martín,3 D. Bouzas-Ramos1

1Department of Physical and Analytical Chemistry, University of Oviedo, Oviedo, Spain – costalesmaria@uniovi.es
2Department of Physical Chemistry, University of Vigo, Vigo, Spain – sgg@uvigo.es
3Department of Organic and Inorganic Chemistry, University of Oviedo, Oviedo, Spain

Keywords: hydrogen bonds, IQA, chemical bond

Classically, hydrogen bonding has been described to play a critical role on the interactions in both organic and inorganic frameworks involving electron withdrawing and/or electron attracting groups. Similarly, it is well known that this type of bonding dominates the net binding interaction within different fields including molecular self-assembly, host-guest chemistry, supramolecular chemistry and molecular docking [1]. Additionally, the existence of hydrogen bond mediated catalysis in different chemical process such as acid rain formation or tautomerization reactions has been recently reported [2].

The amino-imino tautomerization reaction of simple aromatic organic molecules such as functionalized pyridines is well-known to easily proceed by photochemical means. On the other hand, the large activation energy of these reactions in the fundamental state unables the spontaneous tautomerization of these molecules at room temperature [3]. In order to understand the effect of the catalytic activity of hydrogen bonding in the amino-imino -carboxylic acid assisted- tautomerization reaction, a family of 2-aminopyridines has been studied by means of DFT and TD-DFT calculations. All these calculations were supported by spectroscopic experimental findings, by analyzing the main absorption and fluorescence emission bands which allow us to identify the processes involved in the reaction.

In accordance to these calculations, hydrogen bonding assistance of simple carboxylic acids, such as formic or acetic acids, reduces dramatically the activation energy of the studied reaction. Thus, this catalytic effect allows the spontaneous tautomerization reaction of these amino derivatives to take place in the fundamental state.

These results validate and prove the catalytic activity of these weak intermolecular forces in such simple reactions, which furthermore might be extended to more complex ones.

Acknowledgements

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Sila-ibuprofen and interaction densities in crystal vs. enzyme environments

Simon Grabowsky,1 Florian Kleemiss1

1 University of Bremen, Department 2 – Biology/Chemistry, Institute of Inorganic Chemistry and Crystallography, Bremen, Germany – simon.grabowsky@uni-bremen.de

Keywords: sila-ibuprofen, protease inhibitors, non-covalent interactions, environmental effects

A carbon-silicon switch is an established principle in drug design,[1] where a carbon atom of a known drug is exchanged by a silicon atom with the aim to improve the biological properties of the molecule. The rationale behind it is that the molecular shape will not be altered significantly, so that the molecule will fit into the same active sites, but the Si-H bond has reversed polarity compared to the C-H bond (umpolung principle), so that the intermolecular interactions with the biological environment are affected. We have tested this principle using ibuprofen in that we synthesized sila-ibuprofen and derived the electrostatic properties of both ibuprofen and sila-ibuprofen (Figure 1) from high-resolution low-temperature single-crystal synchrotron X-ray diffraction data sets using X-ray wavefunction refinement [2].

We have modelled the intermolecular interactions of both ibuprofen and sila-ibuprofen inside the crystals of the pure substance and inside cyclooxygenase-2 (COX-2) starting from a known protein crystal structure of ibuprofen with COX-2 [3]. We used quantum crystallographic methods, molecular dynamics simulations and QM/MM calculations. Individual atom-atom contacts, the averaged non-covalent interaction (NCI) index, and the interaction density were analyzed. The results are compared to similar results for a different biologically active compound: E64c, a cysteine protease inhibitor.[4,5]

In fact, some interesting differences between ibuprofen and sila-ibuprofen emerged during this study that could potentially lead to sila-ibuprofen having much improved pharmacological properties than regular ibuprofen. Therefore, we precisely determined the solubility of sila-ibuprofen in water (about 5x higher than ibuprofen), tested the pain-regulating effect against rodents (about 10x better pain release in rats than ibuprofen), and the toxicological properties (non-toxic and no inhibition of cell proliferation). We attempt to link the understanding of the intermolecular interactions in the crystal and enzyme to the biological properties.
Fig. 1 Electrostatic potentials derived from X-ray wavefunction refinement mapped onto 0.01 eÅ⁻³ electron-density isosurfaces of both ibuprofen and sila-ibuprofen.

Acknowledgements

We thank many collaboration partners and co-workers who have contributed significantly to this study. We will mention all of them by name in the talk.

References

In good experiments we can trust!

Dietmar Stalke, Regine Herbst-Irmer

Universität Göttingen, Institut für Anorganische Chemie, Göttingen, Germany; dstalke@chemie.uni-goettingen.de, rherbst@chemie.uni-goettingen.de

Keywords: empirical data correction, 3 \( \lambda \) correction, anharmonicity, TDS, overfitting

In this talk we describe recent developments concerning data and model quality in experimental charge-density investigations at a personal view-point. Data quality is not only achieved by the high resolution, high \( I/\sigma(I) \) values, low merging \( R \) values and high multiplicity. Especially the quality of the innermost reflections is crucial for mapping the density distribution of the outermost, valence electrons. New sources seem to be promising improvements. [1] Empirical corrections to correct for low energy contamination of mirror focused X-ray data [2] and for resolution- and temperature-dependent errors caused by factors such as thermal diffuse scattering are described. Shashlik like residual density patterns can indicate the need for an anharmonic description of the thermal motion of individual atoms. [3] The physical reliability of the derived model must be thoroughly analysed. The treatment of hydrogen atoms has been improved by methods to estimate anisotropic thermal motion. For very high resolution data the polarization of the core density cannot be neglected. Several tools to detect systematic errors are described. A validation tool is presented that easily detects when the refinement of additional parameters yields a real improvement of the model or simply overfits the given data. [4] In all investigated structures, we proved that the multipole parameters of atoms with a comparable chemical environment should be constrained to be identical. The use of restraints could be a promising alternative.

**Figure 1:** 3\( \lambda \) correction

**Figure 2:** TDS correction
References

Libraries of extremely localized molecular orbitals and their coupling to Hirshfeld atom refinement

Alessandro Genoni, 1 Lorraine Andrade Malaspina, 2 Benjamin Meyer, 1 Simon Grabowsky 2

1 CNRS & University of Lorraine, Laboratory of Theoretical Physics and Chemistry (UMR CNRS 7019), Metz, France - Alessandro.Genoni@univ-lorraine.fr
2 University of Bremen, Institute of Inorganic Chemistry and Crystallography, Bremen, Germany

Keywords: Extremely Localized Molecular Orbitals, Hirshfeld Atom Refinement, transferability, libraries, protein refinement

Refining crystallographic structures of macromolecules is an important and difficult challenge of crystallography. This is especially true now that more and more sub-atomic and ultra-high resolution X-ray datasets of very large systems started appearing due to recent and impressive advances from the experimental and technological points of view. Therefore, it is clear that, in this context, the use of refinement techniques able to fully exploit the information content of these high-resolution X-ray datasets is fundamental.

One plausible choice would be the emerging Hirshfeld Atom Refinement (HAR) [1], a quantum mechanics-based strategy that, using only X-ray diffraction data, enables to locate the hydrogen atoms positions with the same precision and accuracy of neutron diffraction measurements, even at resolutions as low as 0.8 Å [2]. Nevertheless, HAR requires a tailor-made quantum mechanical calculation at each iteration, which makes its computational cost increase with the size of the system under exam and which consequently prevents its straightforward extension to macromolecules. To overcome this drawback, one possibility is to couple HAR with the new libraries of Extremely Localized Molecular Orbitals (ELMOs).

In fact, ELMOs are orbitals strictly localized on small molecular fragments (e.g., atoms, bonds or functional groups) [3] and, for this reason, also easily transferable from molecule to molecule [4,5]. Following a sort of LEGO approach, databanks of ELMOs have been recently constructed [6]. Now these libraries cover all the possible subunits of the twenty natural amino acids and allow instantaneous reconstructions of wave functions and electron densities of polypeptides and large proteins.

In this talk, the new libraries of ELMOs and the associated program for the automatic transfer of the orbitals [6] will be presented by illustrating both their main features and their current advantages and limitations. Afterwards, the recent coupling of the ELMO-libraries with the Hirshfeld Atom Refinement [7] will be introduced and some encouraging preliminary results obtained from refinements of crystallographic structures of relatively small systems will be shown and discussed in detail.
References

Comparison of experimental and theoretical results of electronic structure of 3-(2'-tetrahydropyranoyloxy)-4-methylthiazole-2(3H)-thione

Jozef Kožíšek, 1 Julia Koziskova, 1 Lukáš Bučinský, 1 Barbara Vénecová, 1 Mike Müller, 2 Jens Hartung 2

1 Slovak University of Technology in Bratislava, Institute of Physical Chemistry and Chemical Physics, Bratislava, Slovakia – jozef.kozisek@stuba.sk
2 Technische Universität Kaiserslautern, Fachbereich Chemie, Organische Chemie, Kaiserslautern, Germany – hartung@chemie.uni-kl.de

Keywords: quantum crystallography, Hirshfeld atom refinement

The title compound is an O-ester structurally deriving from heterocyclic thiohydroxamic acid 3-hydroxy-4-methylthiazole-2(3H)-thione (see Figure 1). When heated in the presence of organic peroxides or azo compounds as chemical initiators, the nitrogen-oxygen bonds in 3-alkoxy-4-methylthiazole-2(3H)-thiones breaks homolytically to yield oxygen-centred radicals in unprecedented specificity. Increasing steric demand at oxygen along the sequence primary, secondary, and tertiary alkyl surprisingly shortens the nitrogen oxygen bond in O-alkyl thiohydroxamates pointing to an unknown stabilizing electronic effect induced by steric demand. This responsivity is particularly significant for thiazole-2(3H)-thione-derived cyclic thiohydroxamic acids. In order to correlate N,O-bond lengths to changes in electron distribution and thus experimental bond order, we started to investigate 3-hydroxy-4-methylthiazole-2(3H)-thione by low-temperature X-ray and analyzed the data in Bader’s Atoms in Molecule Model (AIM) [1].

The crystal and electronic structure of 3-(2'-tetrahydropyranoyloxy)-4-methylthiazole-2(3H)-thione, C₉H₁₃NO₂S₂, has been determined and analyzed in terms of connectivity and packing patterns. The compound crystallizes in the monoclinic crystal system in the space group P2₁/n.

Data collection was performed on a Stoe STADIVARI diffractometer with a Dectris Pilatus 300K detector and with an Incoatec IμS Ag microfocus source (Ag-Kα, λ = 0.56083 Å) at 100 K using a nitrogen gas open-flow cooler Cobra from Oxford Cryosystems. Data reduction was processed using X-Area [2]. For numerical absorption corrections a crystal-shape model with 17 faces was employed. Resolution 0.37 Å, an average redundancy of 14.29 gives R_{int} of 7.22%. Multipolar refinement was performed on F² using XD suite of programs. The preliminary results shows that both N1 and O1 atoms are negatively charged and that the Laplacian has small positive value (see Figure 2) [3]. In contradiction, the theoretical assessment (B3LYP/6-311G*) of the electronic structure yields a negative value of the Laplacian, of ca. -5 e.Å⁻⁵. Nevertheless, what have the results in common are the large values of the Hessian eigenvalues, which agree well with each other. Hence, the common features as well as the differences between the multipolar and theoretical of charge density shall be critically highlighted.
Fig. 1. Atom numbering

Fig. 2. 3D plot [3] of the Laplacian of electron density at isosurface value of 15.0 e/Å$^5$

Acknowledgement

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References

Quantum crystallography (QCr): Early views & recent ideas

Lou Massa

Hunter College, and the PhD program of the Graduate Center, City University of New York. lmassa@hunter.cuny.edu, (Tel.: +1 (718) 873 4535).

Keywords: X-ray intensity data, the electron density. Projectors, N-representability, The Clinton iterative matrix equations

It is possible to transform X-ray diffraction data into an electron density arising from an antisymmetric N-electron wave function. A formalism to accomplish this employs a constrained idempotent one-body density matrix \( P \). The formalism delivers single determinant N-representability. By minimizing \( \text{Tr} (P^2 - P)^2 \) subject to X-ray scattering constraints, one obtains the Clinton matrix equations of the form:

\[
P_{n+1} = 3P_n^2 - 2P_n^3 + \sum_k \lambda_k(n)O_k
\]

where \(-\lambda_k\) is the \( k^{th} \) Lagrangian multiplier for constraint \( \text{Tr} PO_k = \langle \hat{O}_k \rangle \), & where \( \langle \hat{O}_k \rangle \) is the expectation value of the X-ray scattering observable \( O_k \). Examples with crystals show that N-representable one body density matrices can be extracted from X-ray scattering data. How to proceed with this formalism to biological molecules will be discussed.

Fig. 1  Sketch related to defining N-representability of density matrices.

References
Experimental and theoretical structure factors of simple metal oxides

Eiji Nishibori,¹ Hidetaka Kasai¹

¹ University of Tsukuba, Division of Physics, Faculty of Pure and Applied Sciences & Tsukuba Research Center for Energy Materials Science, Tsukuba, Japan – nishibori.eiji.ga@u.tsukuba.ac.jp

Keywords: Structure factor, SR powder diffraction, theoretical calculation, metal oxides

Simple metal oxides are one of the most important materials in our human life. They are widely used in the practical application in many fields such as electronic device, illumination, and magnet. They are also used in the research of advanced condensed matter physics due to their exotic properties, multiferroics and superconductivities, etc. Furthermore, they have attracted interests as energy materials such as, butty and solar cell.

Some of simple metal oxides with transition metal are classified as strongly correlated electron system. In such system, it is difficult to design and elucidate the electronic structure and properties by theoretical calculation. Systematic charge density study of metal oxides by X-ray diffraction will create a chart for the development and improvement of materials.

Recently, several kinds of theoretical calculation packages are available for not only theoretician but also experimental scientists. WIEN2k [1] and CRYSTAL [2] packages are well-known in the fields of X-ray charge density. These packages can calculate X-ray structure factors from a charge density determined by theoretical calculation. Many kinds of theoretical method including LDA, GGA, LDA+U and Orbital polarization method can be used in the WIEN2k. Hartree Fock, density functional or various hybrid approximations (global, range-separatated and double-hybrids) can also be used in CRYSTAL program. The charge density calculated by these packages using different methods, potentials, and parameters have small discrepancies. The discrepancies should also recognize structure factors.

We measured accurate structure factors of simple metal oxide system, such as Al₂O₃, ZnO, TiO₂, and Cr₂O₃ from powder diffraction data at SPring-8. The set of powder sample is Standard Reference Materials (SRM) 674 X-ray powder diffraction intensity set of National Institute of Standards and Technology. These are quantitative powder diffraction standard that is suitable for charge density study. We reported the results of multipole refinement for TiO₂ and Al₂O₃[3]. Systematic charge density study of these materials will provide important clue for deep understanding of electronic structure of transition metal system.

Powder sample were agglomerated by small amounts of glue. The agglomerated sample was cut a rectangle with 3 × 0.3 × 0.3 mm dimension. The powder profiles were measured at 100K using N₂ gas flow low temperature device. We measured two powder diffraction data for ZnO and Cr₂O₃ to improve counting statistics of high order data.

We did Rietveld refinement of TiO₂, Al₂O₃, ZnO and Cr₂O₃ to extract observed structure factors and make sure the quality of the data. Figures 1 show the fitting results of Rietveld refinement for (a) ZnO and (b) Cr₂O₃. The reliability factors based on Bragg intensities were as small as 1.7 % and 3.0%, respectively. There are several discrepancies between observed and calculated data in low angle region less than 10° in 2θ for ZnO and around 10° in 2θ for Cr₂O₃. No such
discrepancies observed in middle angle region as shown in the figures. We already reported the fitting results of TiO$_2$ and Al$_2$O$_3$ in the previous study [3]. The qualities of fittings for ZnO and Cr$_2$O$_3$ are almost comparable to those of TiO$_2$ and Al$_2$O$_3$.

![Graph](image1)

(a)

![Graph](image2)

(b)

Fig. 1 The Fitting results of Rietveld Refinement for (a)ZnO and (b)Cr$_2$O$_3$.

We did multipole refinements for TiO$_2$, Al$_2$O$_3$ and ZnO using program XD [4]. The reliability factors were R=0.94% for TiO$_2$, R=1.17% Al$_2$O$_3$ and R=0.79% for ZnO. The multipole refinement
of Cr$_2$O$_3$ is now in progress. The qualities of structure factors for three of four materials were detailed charge density study.

We also calculated structure factors of TiO$_2$, Al$_2$O$_3$, ZnO and Cr$_2$O$_3$ using WIEN2k and Crystal packages using several kinds of method. Detailed comparison between experiment and theory will be presented at the conference.

Acknowledgements

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References

A method to estimate statistical errors of properties derived from charge density modeling

Bertrand Fournier,^1^ Benoit Guillot,^2^ Claude Lecomte,^3^ Eduardo C. Escudero-Adán,^4^ Christian Jelsch^5^

^1^ Laboratoire de Physique Pharmaceutique, Univ. Paris Sud, Châtenay-Malabry, France bertrand.fournier@u-psud.fr
^2^ Laboratoire CRM2, Université de Lorraine, Vandoeuvre les Nancy, France benoit.guillot@univ-lorraine.fr
^3^ Laboratoire CRM2, Université de Lorraine, Vandoeuvre les Nancy, France claude.lecomte@univ-lorraine.fr
^4^ The Barcelona Institute of Science and Technology, ICIQ, Tarragona, Spain eescudero@iciq.es
^5^ Laboratoire CRM2, Université de Lorraine, Vandoeuvre les Nancy, France christian.jelsch@univ-lorraine.fr

Keywords: uncertainties, electron density properties, charge density model, least-squares, topology

Estimating uncertainties on properties derived from a charge distribution model is essential to avoid any false or over-interpretation of these properties. This is especially true when experimental information is meant to be included in a quantitative comparison, for instance with results obtained from theoretical calculations or from quantum crystallography methods. Hence we propose a methodology, implemented in the program MoProSuite [1], designed to estimate uncertainties on structural and charge density derived properties. This method is based on calculation of sample standard deviations of properties values obtained using randomly deviating charge density models [2]. The parameter shifts applied in the deviating models are generated in order to respect the variance-covariance matrix issued from the least squares refinement. This procedure can, fundamentally, be applied to any electron density derived property. This includes electron density itself, but also topological descriptors such as critical point coordinates, Laplacian, ellipticity at critical points and charges integrated over atomic basins. Errors on electrostatic potentials and interaction energies are also available through this procedure. The method will be first exemplified with the charge density of compound (E)-5-Phenyl-pent-1-enyl-boronic acid, refined at 0.45 Å resolution. Effects on properties uncertainties of model quality, data resolution and data collection temperature will also be discussed.

References

Methods development for charge density studies of actinide compounds: From data reduction to model building

Christopher G. Gianopoulos,¹ Vladimir V. Zhurov,¹² A. Alan Pinkerton³

¹ University of Toledo, Department of Chemistry and Biochemistry, Toledo, Ohio USA – chris.gianopoulos@utoledo.edu
² University of Toledo, Department of Chemistry and Biochemistry, Toledo, Ohio USA – vladimir.zhurov@utoledo.edu
³ University of Toledo, Department of Chemistry and Biochemistry, Toledo, Ohio USA – a.pinkerton@utoledo.edu

Keywords: bonding in actinides, charge density, high-resolution x-ray diffraction

Charge density studies of small molecules have shown that highly accurate experimental electron densities can be afforded from carefully measured high-resolution X-ray diffraction data. However, obtaining accurate electron density distributions from heavy-atom containing systems is a considerable challenge. To this end, we have set out to develop methods for accurate charge density studies of actinide compounds from X-ray data measured at low temperature (20 K) and have previously reported such a study for [PPh₄][UF₆] [1] and Cs₂UO₂Cl₄ [2]. In this context, the following presentation will describe the improvements we have made in this area concerning data collection, reduction and modeling via an augmented Hansen-Coppens scheme. Splitting of the actinide pseudo-atom based on an appropriate choice of radial functions for multipole expansion is crucial. Our experiments demonstrate that definition and treatment of the frozen core (60 electrons), outer core (n ≥ 5) and valence electron distributions are necessary in order to obtain accurate results. The experimental description of actinide-element bonding, from the perspective of Bader’s Quantum Theory of Atoms in Molecules, will also be discussed and compared with analogous theoretical results.

Fig. 1 Experimental deformation density maps for the UF₆⁻ ion depicting (left) charge concentrations only and (right) total deformation density, isosurfaces drawn at ±0.15 e/Å³ with charge concentrations in blue and depletions in red.

References

Removing residual bond density in organic molecules: A technical note

Alexander Y Nazarenko

1 State University of New York, College at Buffalo, Chemistry Department, Buffalo, NY, USA – nazareay@buffalostate.edu

Keywords: Hirshfeld atom refinement, independent atom modelling, X-ray structure, virtual atom

The Independent Atom Model (IAM) is based on assumption that the electron density is well described by the spherically averaged density of the isolated atoms. It is a good estimate for the atoms for which the valence electron density is a minor part of the total. IAM is less successful for light atoms: when the quality of structure is reasonably good, you can see areas of bond-related residual positive density located on C-C, C-N and C=O bonds. With resolution better than 0.6-0.5 Å, these peaks can be higher than 0.4 e/Å³; R-factor and goodness of fit are abnormally large. Controversially, this discourages high resolution measurements!

To reduce the bias coming from bond density, Hirshfeld atom refinement (HAR) [1] was employed. A number of structures of various organic and element-organic molecules were tested. The quality of the datasets being tested was not sufficient for applying charge density formalism; therefore, only geometrical parameters (bond lengths and angles and their estimated uncertainties) were compared.

As a simple alternative, we employ an empirical approach using usual IAM software (SHELXL-201X, Jana2006). Scattering centers are placed at fixed calculated positions between C, N, and O atoms, with ‘occupancies’ being different for single, double, aromatic and triple bonds. Scattering is approximated by a single Gaussian which can be possibly justified by a small value of correction. These ‘atoms’ are treated as isotropic: multiplication of scattering Gaussian by Debye-Waller factor yields one Gaussian function to describe both effects. The number of introduced parameters can be as low as one (for overall occupancy of pseudo-atom part of the structure). Introduction of virtual atoms makes the effect similar to one hydrogen atom per 4-5 C-C bonds, which is significant enough to justify the effort. Alternatively, each bond can be treated separately (number of additional parameters is roughly equal to the number of bonds). This leads to further improvement. This approach is similar to suggested in numerous publications with paper [2] being one of the first.

Visible improvement of fitting characteristics was achieved with both methods, especially for molecules with aromatic fragments. Some representative examples: Biphenyl, resolution 0.57 Å, before correction R=0.059, after 0.036. Diphenylacetylene, 0.58 Å: before correction R=0.048, S=1.04; after R=0.026, S=1.02. Dimethyl-3,4,5,6-tetraphenylcyclohexa-3,5-diene-1,2-dicarboxylate, 0.80 Å, Cu radiation (!): before R=0.035, S=1.04; after R=0.026, S=1.03. trans-[3-(3-nitrophenyl) oxiran-2-yl](phenyl)methanone, 0.58 Å: before R=0.046, after 0.032. Ylide, 0.48 Å: before R=0.027, after 0.018. Uncertainties of bond distances are also visibly lower. This enable us to remove most of residual bond density from the Fourier difference map allowing then to address other sources of deviation such as disorder and, of course, experimental and data processing limitations.
Our current limited experience proves Hirshfeld atom refinement helpful even for routine crystal structure refinement where no charge density study was intended. Running HAR after successful IAM refinement indirectly helps to encourage high quality data collection.

References

Evaluation of spatial domains

Miroslav Kohout 1

1 Max Planck Institute for Chemical Physics of Solids, Dresden, Germany – kohout@cpfs.mpg.de

Keywords: space partitioning, QTAIM

The evaluation of bond descriptors in real space is usually performed over regions determined by an exhaustive space partitioning [1]. Thus, the choice of suitable prescription for the partitioning is of great importance. On the basis of the electron density gradient field the QTAIM domains [2] are created and widely used as the spatial representation of an atom within a molecular or solid state system. A finer structure of the bonding situation can be examined using the electron localizability indicator ELI-D utilizing spatial domains based on the gradient field of ELI-D [3], in analogy to the QTAIM partitioning. The impact of the space partitioning on the definition of structural subunit as well as the influence of the domain evaluation on the resulting analysis of the system will be discussed.

References

Characterizing the halogen and chalcogen bonds in crystals: PAEM vs ESP

Ekaterina Bartashevich,¹ Svetlana Mukhitdinova,¹ Vladimir Tsirelson²

¹ South Ural State University, Department of Chemistry, Chelyabinsk, Russia – bartashevichev@susu.ru
² D.I. Mendeleev University of Chemical Technology, Moscow, Russia – tsirel@muctr.ru

Keywords: potential acting on an electron in a molecule, halogen bond, chalcogen bond

We examined the features of the electrostatic potential (ESP) and the potential acting on an electron in a molecule (PAEM) [1, 2]. Unlike the ESP, the PAEM contains both classic and quantum components. For analysis of the halogen and chalcogen bonding features, the considered functions were mapped on the different sides of the closed RDG isosurface [3] placed between non-covalently interacting atoms. We found that on the side of the electron-donor atom, the region of non-covalent interactions is characterized by the potential acting on an electron, and on the side of the σ-hole it is described by the electrostatic potential acting on the unit positive charge [4].

Fig. 1 Distributions of –ESP and PAEM mapped on the isosurface of RDG =0.5 and 1D functions along the halogen bond N…Cl in the complex NH₃…ClF

Thus, a combination of these tools is proposed for the halogen and chalcogen bonding identification. Moreover, a comparison of the distributions of these functions on the isosurface of the electron density (ED) for the halogen and chalcogen atoms carried out. The account for the exchange-correlation interaction in PAEM retains the specific anisotropy of the electrostatic
potential, which is commonly used for explanation the halogen bonding with reliance on σ-hole concept. Along the halogen bonds, the curvatures of -ESP and PAEM functions are opposite: from the electron donor atom ESP increases more steeply, while from the halogen atom the sharper increase is observed for PAEM function. The functions -ESP and PAEM mapped on the closed isosurface of the reduced density gradient significantly differ from the side facing the halogen atom and from the side, looking at the electron donor atom. The relative positions of -ESP$^{\text{max}}$ and PAEM$^{\text{max}}$ functions along the halogen bond line help to distinguish which atom is the halogen bond donor, and which is the acceptor, while the values of PAEM$^{\text{max}}$ correlate with the electron delocalization indices.

![Fig. 1 Distributions of – ESP and PAEM mapped on the isosurfaces of ED=0.001 a. u., for ICl, BrCl, Cl2, CIF molecules](image)

In crystals, the typical non-covalent halogen and chalcogen bonds accompanied by the complicated mutual orientations of anisotropic features of the halogen/chalcogen atoms. The standard geometrical criteria are not enough to distinguish the type of bonding and to recognize which atom is a donor or which is an acceptor of electrons in such cases. A methodology that suggests the use of -ESP and PAEM functions jointly copes with this problem successfully.
Acknowledgements

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Charge density analysis of triphosphazenes: Aromaticity and the NCl$_2$ unit.

Fernando Cortés-Guzmán,*1,2 Vojtech Jancik,*1,2 Regine Herbst-Irmer,3 Diego Matínez-Otero$^{1,2}$

1 Instituto de Química, Universidad Nacional Autónoma de México, México, D.F., México – fercor@unam.mx
2 Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Toluca, Estado de México, México – vjancik@unam.mx
3 Institut für Anorganische Chemie, Universität Göttingen, Göttingen, Germany

Keywords: experimental electron density, inorganic aromaticity, hyperconjugation, supramolecular chemistry, unit transferability

Experimental charge density studies of hexachloro-cyclo-triphosphazene (P$_3$N$_3$) and the boat conformation of octachloro-cyclo-tetraphosphazene (P$_4$N$_4$) were performed to describe the origin of the electron delocalization in these rings.[1] The experimental results were compared to theoretical ones in the solid state and a gas phase. Electron density analysis revealed a highly polarized nature of the P–N bonds and a modular structure of the P$_3$N$_3$ and P$_4$N$_4$ rings, which can be separated into independent Cl$_2$PN units with a perfect transferability between both rings. The analysis of the experimental source function[2] shows the presence of negative hyperconjugation involving both out-of-plane and in-plane nitrogen electrons as well as electrons of the chlorine atoms. These results discard the presence of pseudoaromatic delocalization in the nearly planar P$_3$N$_3$ ring. The study of P$_3$N$_3$Cl$_6$ also revealed the presence of a NCl$_2$ synthon within the crystal formed by a nitrogen and two chlorine atoms from three different molecules with a cyclic sequence of charge concentration and charge depletion interactions, where nitrogen acts simultaneously as a donor and acceptor in closed shell interactions with the chlorine atoms. The observed NCl$_2$ synthon is a homologue of the X$_3$ unit reported for halogen bonding. [3]

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References

How real-space bonding indicators can help in description of the nature of donor acceptor bonds

Lilianna Chęcińska¹

¹ University of Lodz, Faculty of Chemistry, Lodz, Poland – lilianna.checinska@chemia.uni.lodz.pl

Keywords: bonding indicators, electron density, dative bonds, Lewis complexes, atoms in molecules, electron localizability indicator

Lewis pair complexes between main group element compounds have witnessed a remarkable renaissance in recent years [1]. The studies consider not only the synthetic and application aspects but are also directed the focus on the nature and proper Lewis formula description of the donor acceptor bonds [2-4]. Beyond molecular complexes, for which the bonding situation is unclear, the increase of interest concerns the so-called dative bonds. In the literature, the debate is still active “how to distinguish formally dative bond from covalent or polar ones”.

The nature of some disputable types of chemical connections (as an example see Fig. 1) has been subjected to analyze real-space bonding indicators (RSBIs) derived from the theoretically or/and experimentally calculated electron densities and electron pair densities. It is a set of topological and integrated parameters obtained by using the Atoms In Molecules (AIM) [5] and Electron Localizability Indicator (ELI-D) [6] space partitioning schemes, which divide space in basins of atoms and paired electrons, respectively.

![Fig. 1 Molecular graph (left, AIMAll [7] graphic) and ELI-D localization domain representation (right, MolIso [8] graphic at isovalue Y=1.50) of gas-phase structure of [Me₃SiOPMe₃]+.](image)

References

Stacking of planar polyenic rings: from dispersion interactions to multicentric two-electron covalent bonding

Krešimir Molčanov, Biserka Kojić-Prodić

1 Rudjer Bošković Institute, Zagreb, Croatia – kmolcano@irb.hr

Keywords: π-stacking, aromaticity, quinones, semiquinone radicals, metal-chelates

Stacking of aromatic rings is a well-known type of intermolecular interaction and has found its way into textbooks on supramolecular chemistry [1,2]. It is usually considered as rather weak (typically <1 kcal mol⁻¹) interaction, and that stacking is an exclusive property of aromatic rings; the fact that other types of planar conjugated rings also stack is usually overlooked. Misconceptions about the very nature of stacking are also numerous, and are reflected in a variety of names used, which are often misleading: π····π interaction, π-stacking, π-interaction, aromatic interaction, stacking interaction, etc.

However, there is a growing amount of evidence that all rings stack, and that aromaticity is not a conditio sine qua non for formation of π-stacks [3]. Stacking of planar organic radicals is known and has been used in design of organic semiconductors and magnetic materials [4]. Our detailed studies have shown that interactions between quinoid rings [5] and semiquinone radicals [7,6] are by an order of a magnitude stronger than interactions between aromatic rings.

As a result of numerous X-ray charge density studies on different types of stacked rings [5-7], we propose a generalised model of stacking, which accounts for both aromatic and non-aromatic rings. It is primarily based on our experimental X-ray charge density data of quinoid and semiquinoid rings and supported by quantum chemical computations [5-7]. Our results show that: 1) non-aromatic planar polyenic rings can stack, 2) interactions are more pronounced between systems/rings with little or no π-electron delocalisation (e.g. quinones) than those involving delocalised systems (e.g. aromatics), 3) the main component of the interaction is electrostatic/multipolar between closed-shell rings, whereas 4) interactions between radicals involve a significant covalent contribution. Thus, stacking covers a wide range of interactions and energies ranging from weak dispersion to non-localised two-electron multicentric covalent bonding (‘pancake bonding’).

Acknowledgements

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References


What does electron density analysis tell us about bonding in transition metal-doped boron and carbon clusters?

N. Sukumar,1 Pinaki Saha,2 Amol B. Rahane,3 Rudra Agarwal,4 Vijay Kumar5

1 Department of Chemistry and Center for Informatics, Shiv Nadar University, Dadri, India – n.sukumar@snu.edu.in
2 Department of Chemistry, Shiv Nadar University, Dadri, India – ps630@snu.edu.in
3 Dr. Vijay Kumar Foundation, Gurgaon, India – amol_rahane2000@yahoo.com
4 Department of Chemistry, Shiv Nadar University, Dadri, India – ra298@snu.edu.in
5 Dr. Vijay Kumar Foundation, Gurgaon & Center for Informatics, Shiv Nadar University, Dadri, India – vijay.kumar@snu.edu.in

Keywords: electron density analysis, boron clusters, carbon clusters, electron delocalization, structural stability

Although the nature of the chemical bond is at the heart of chemistry, chemists often work with several distinct conceptions of the chemical bond, which are not necessarily compatible with each other. The Lewis concept of the electron pair bond [1] is now over a century old, predating the quantum mechanical theory of bonding in molecules. We now recognize electron pairing to be a consequence of the Pauli exclusion principle and the associated Fermi hole. The traditional Lewis electron pair bond concept has been extended to admit the possibility of 3-center, 2-electron bonds in “electron deficient” boranes, and subsequently further extended, using AdNDP analysis [2] (an extension of natural bond orbitals NBO analysis), to include n-center (but always 2-electron) objects (with n arbitrarily large). An alternate to such orbital treatments is provided by examination of topological features of the electron density, such as bond paths (gradient paths of the electron density) connecting pairs of nuclei. Such bond paths are not associated with a fixed electron count. However, as has been pointed out by several authors [3,4], the mere existence of a bond path between a pair of nuclei does not signify the existence of a chemical bond between them or indicate the strength of the interaction. Double integration of the Fermi hole density over spatial regions provides a valid measure of electron localization and delocalization [5]. One can also conceive of the chemical bond as a force that holds a pair of atoms together, quantified by the dissociation energy required to break the bond. While this works well for simple diatomics, the correlation between dissociation energy and electron count or the electron density between a pair of nuclei is not straightforward for open shell systems or polyatomic molecules.

The divergence between these different conceptions of the chemical bond is particularly dramatic for “electron deficient” boron compounds and for metallic nanoclusters, where extensive electron delocalization and multi-center bonding are prevalent. Nevertheless, combining information from topological features of the electron density with orbital-based models allows meaningful chemical conclusions about bonding to be drawn, even for unusual molecular systems.

Here we have analyzed trends in bonding and stability for several clusters including ring-shaped clusters for boron and carbon as well as drum-shaped and fullerene-like clusters of boron, from computed ab initio electron density distributions, and investigated the effects of transition metal (TM) doping on their structural and physical properties. Analysis of the electron density at bond and ring critical points, the Laplacian of the electron density, the electron localization function [6], the source function [7], and localization-delocalization indices, all indicate the coexistence of covalent bonds and delocalized charge distribution in boron clusters [8]. Rings of carbon atoms too seem to be stabilized by metal coordination for selected sizes and electron counts. For drum-shaped \( M@B_{14} \) (\( M = a 3d \) TM atom) and \( M@B_{16} \) (\( M = 3d, 4d, \) and 5d TM atom) clusters,
our results suggest two- and three-center $\sigma$ bonding within and between two B7/B8 rings, respectively, and hybridization between the TM d orbitals and the $\pi$ bonded molecular orbitals of the drum. Assembly of Co@B$_{14}$ clusters has been shown to stabilize a metallic Co atomic nanowire within a boron nanotube [9].

We have also studied metal atom encapsulated fullerene-like boron cage structures and shown that Cr@B$_{20}$ is the smallest cage for Cr encapsulation, while B$_{22}$ is the smallest symmetric cage for Mo and W encapsulation. Electron density and molecular orbital analysis suggests that Cr@B$_{18}$, Cr@B$_{20}$, M@B$_{22}$ (M = Cr, Mo, and W) and M@B$_{24}$ (M = Mo and W) cages are stabilized by 18 $\pi$-bonded valence electrons, whereas the drum-shaped M@B$_{18}$ (M = Mo and W) clusters are stabilized by 20 $\pi$-bonded valence electrons [10]. We have also studied larger boron clusters in the size range 68-74 and shown that the global minimum structure for B$_{70}$ is a tubular structure, which is nearly degenerate with a quasi-planar structure having three hexagonal vacancies [10]. Analysis of a large number of atomic clusters, of various shapes and sizes, indicates a broad parallelism between different measures of bonding and localization in these clusters.

Fig. 1 Electrostatic potential of (a) Cr@B$_{22}$ and (b) tubular B$_{70}$ cluster mapped onto a $\rho(r) = 0.1$ e/Bohr$^3$ electron density isosurface. Blue regions indicate negative electrostatic potentials associated with the boron atoms. (b) Contour plot of the Laplacian of Cr@B$_{22}$ cluster in a plane passing through atoms B7, B8, B15, B16, B21, B22, and Cr. Solid (dashed blue) contours indicate positive (negative) values of $L = -\nabla^2\rho(r)$. 
Acknowledgements

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References

Spin-resolved momentum densities: What we can learn from magnetic Compton scattering

Jon Duffy

1 University of Warwick, Department of Physics, Coventry, CV4 7AL UK, j.a.duffy@warwick.ac.uk

Keywords: Spin densities; Compton scattering; magnetism; electronic structure.

Studies of spin-resolved electron momentum densities involve the measurement of the so-called magnetic Compton profile. This is a one-dimensional projection of the electron momentum distribution of only those electrons that contribute to the spin moment of a sample. The technique is applicable to ferri- and ferromagnetic materials. The profile is obtained via the inelastic “Compton” scattering of high energy X-rays (typically ~200 keV). For the work presented here, the ESRF and SPring-8 synchrotron X-ray sources were used. In order to perform our new experiments, an Oxford Instruments Spectromag cryomagnet has been installed for use on the high energy beamline, BL08W. The magnet can provide a sample environment with applied magnetic fields up to 8 Tesla, at temperatures from 1.5 K to 600 K.

Since electrons originating from different atomic orbitals have specific momentum densities, it is often possible to determine the origin of the magnetism present. Typically, interpretation requires the use of electronic structure calculations using molecular orbital and band structure approaches. In this talk, the value of this approach will be demonstrated with some examples of our recent research, including studies of the magnetism in the quantum critical system Sr$_3$Ru$_2$O$_7$ and in the high entropy alloy system NiCoFeCrPd.

Sr$_3$Ru$_2$O$_7$ is considered to be a system that exhibits quantum criticality (for example, see [1] and references therein). It has a low temperature metamagnetic transition which may be related to a change in the topology of the Fermi surface. We measured the spin density at 1.5 K, in the metamagnetic phase. Our initial density functional calculations were fixed to reproduce the value of the experimentally determined spin moment, but do not agree well with the measured spin density. In the talk, we will discuss how it is possible to gain a good agreement with the experimental spin densities from the calculations and the consequences of this in relation to the underlying physics.

The other example to be covered is one of the so-called “high entropy alloys” (for example see references [2,3]). We have studied a series of disordered alloys building to the five-component high entropy system NiFeCoCrPd. For this work we measured this high entropy sample, and also its prototype compounds NiCoFe and NiCoFeCr. We also performed electronic structure calculations to predict the magnetic moments and resultant spin densities. In the talk we will discuss the changes as the number of components increases and also the unexpectedly-isotropic spin density.
Acknowledgements

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References

Advanced spectroscopic characterization of lithium-ion battery materials using X-ray Compton scattering

Hasnain Hafiz, 1 K. Suzuki, 2 B. Barbiellini, 1,3 Y. Sakurai, 4 H. Sakurai, 2 A. Bansil 1

1 Northeastern University, Physics Department, Boston, MA, USA – hafiz.h@husky.neu.edu
2 Gunma University, Faculty of Science and Technology, Kiryu, Gunma, Japan
3 Lappeenranta University of Technology, School of Engineering Science, Lappeenranta, Finland
4 Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo, Japan

Keywords: Lithium-ion battery, Compton scattering, redox orbital

The key reactions underlying the mechanism of Li-ion battery (LIB) materials are the so-called reduction-oxidation (redox) reactions, which are responsible for generating current as conduction electrons from the lithium anode are transferred to the redox orbitals of the cathode. The ability to visualize or image the redox orbitals and how these orbitals evolve under lithiation and delithiation processes is of great fundamental and practical interest for understanding and advancing the battery materials field. In order to develop advanced spectroscopic tools for characterizing LIB materials, we discuss x-ray Compton scattering spectra along with parallel first-principles computations using lithium iron phosphate (LFP) as an exemplar LIB material [1]. The visualization of the redox orbitals in momentum and real spaces reveals relationships between wave function localization, bonding properties, voltage and energy density of the battery. In particular, insight is obtained into how voltage shift is connected with the modification of the bond between the transition metal and the oxygen atoms in the cathode material. We also discuss effects of substituting Fe atoms in LFP by other transition metals such as Mn, Co and Ni as a pathway toward improving the limited energy density of LFP.

References

Nonlinear optical microscopy for discriminating tissues based on ultrastructure

Danielle Tokarz,1 Richard Cisek,2 Sylvia L. Asa,3 Virginijus Barzda,4 Brian C. Wilson5

1 Saint Mary’s University, Department of Chemistry, Halifax, Canada – danielle.tokarz@smu.ca
2 Saint Mary’s University, Department of Chemistry, Halifax, Canada – richard.cisek@smu.ca
3 University Health Network and University of Toronto, Laboratory Medicine & Pathology, Toronto, Canada – sylvia.asa@uhn.ca
4 University of Toronto, Department of Chemical and Physical Sciences, Mississauga, Canada – virgis.barzda@utoronto.ca
5 University of Toronto, Department of Medical Biophysics, Toronto, Canada – wilson@uhnres.utoronto.ca

Keywords: laser imaging, optical crystallography, optical pathology, second harmonic generation, collagen

The early diagnosis of diseases such as cancer is essential for improving survival rates as treating early-stage cancers is often more straightforward and effective than treating late-stage cancers. Typically, cancer diagnosis is performed by visual inspection of tissue biopsies using dyes using a bright-field microscope. However, variability in morphological interpretation of tissue by standard histopathology can be controversial. Therefore, pathologists could benefit in identifying cancer on biopsy or surgical resection sections by using novel automated technologies with high spatial resolution and improved disease specificity.

During cancer initiation and progression, the extracellular matrix (ECM) is often deregulated and becomes disorganized. A strategy towards improved cancer diagnosis is to develop technology by which the structural alterations in the ECM during tumor initiation and progression can be identified and quantified.

Since collagen is a major constituent of the ECM and it consists of triple helices within fibrils, collagen efficiently produces the second-order nonlinear optical effect, second harmonic generation (SHG). Therefore, SHG microscopy can be applied to visualize collagen in the ECM. In general, only molecules and macromolecular structures possessing non-inversion symmetry are able to produce SHG signal. In SHG, two photons of the same frequency interact with matter to produce a single photon of twice the frequency or one half the wavelength of the incoming photon. These nonlinear optical processes only occur efficiently when very high light intensities are used such as that given by a pulsed laser.

Additionally, by performing polarization-sensitive SHG imaging, referred to as polarization-in, polarization-out (PIPO) SHG microscopy, the second-order nonlinear optical susceptibility tensor component ratio, \( \chi^{(2)}_{zzz}/\chi^{(2)}_{zxx} \), and the degree of linear polarization, DOLP, can be measured. The \( \chi^{(2)}_{zzz}/\chi^{(2)}_{zxx} \) is related to the collagen ultrastructure while the DOLP indicates the relative amount of coherent signal and incoherent scattering of SHG. Therefore, PIPO SHG microscopy can be used as a quantitative method to extract changes in the structure of collagen in the ECM. Previously, PIPO SHG microscopy has been demonstrated to reveal changes in the ultrastructure of collagen in non-small cell lung carcinoma [1]. In the present study, we expand the application of PIPO SHG microscopy to investigate other types of cancer, including human pancreatic cancer as well as classical papillary thyroid carcinoma (cPTC) and follicular variant papillary thyroid carcinoma (FVPTC) [2].
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References

Phonon-mediated high-temperature superconductivity?

Roman Krems,¹ John Sous,¹,² Oliver Stauffert,¹ Mona Berciu²

¹ University of British Columbia, Department of Chemistry, Vancouver, Canada – rkrems@chem.ubc.ca
² University of British Columbia, Department of Physics, Vancouver, Canada

Keywords: polaron interactions, bipolarons, phonon-mediated interactions, high-Tc superconductivity

Since the discovery of superconductivity in Hg at a critical temperature 4.2 K, the quest for superconducting materials with high critical temperature has been at the forefront of condensed-matter physics research. While the mechanism of conventional (low-temperature) superconductivity is well understood to be the consequence of phonon-mediated pairing, there is currently no proven theory of high-temperature superconductivity. The general consensus is that phonon-mediated superconductivity cannot exhibit high critical temperatures. This belief is based on the premise that electrons dressed by phonons must have a larger effective mass than the bare electrons and that this effective mass increases with the strength of coupling to phonons. It is therefore believed that pairs of electrons bound by phonons at strong coupling must form heavy quasi-particles that cannot condense into a superfluid at a high temperature. Here, we challenge this premise. We show that if the coupling to phonons modulates the kinetic energy of the electrons -- as in the Su-Shrieffer-Heeger (SSH) model introduced to describe electron pairing in polyacetylene -- then electrons can bind by phonon-mediated interactions into light bipolarons. The effective mass of the phonon-dressed electron pairs remains similar to the mass of two bare electrons at strong coupling to phonons, which should favor a high critical temperature. Thus, phonon-mediated high-temperature superconductivity is, in principle, possible. The question we would like to raise in this talk is: Can one design materials where the electron – phonon coupling is both of the SSH type and strong enough to allow the formation of strongly bound bipolarons?
Design of macrocyclic chelating agents with actinium for development of targeted radiotherapy

Amanda Morgenstern,¹ Enrique Batista,¹ Stosh Kozimor,¹ Laura Lilley,¹ Ben Stein,¹ Ping Yang¹

¹ Los Alamos National Laboratory, Los Alamos, NM, USA. – amorgenstern@lanl.gov

Keywords: Actinides, Chemical Bonding, Radiotherapy, Ligand Design

Actinium-225 is an excellent candidate for targeted radiotherapy to treat cancer and infections due to its half-life of 10 days and emission of four, high energy alpha particles. In order to harness and direct the energetic potential of actinium, strongly binding chelators must be developed that are capable of retaining actinium ions while they find the desired biochemical target. Little work has been done to understand the bonding properties of actinium making the development of chelating ligands a challenging task. In this talk I present theoretical work done in collaboration with experimentalists to elucidate the unique bonding properties of macrocyclic chelating agents varying in ring size, coordination number, and functional groups. Results include both experimentally determined and theoretically calculated charge densities. We first identify the optimal ring size and coordination number of the chelates for actinium binding based on thermodynamic analysis. Using this information, we explore attaching different functional groups to various positions on the rings. We then perform bonding analysis of proposed chelators including orbital decomposition methods and studying the geometry of the electron density. The fundamental bonding information that is gained for actinium through this study can be used as a driving force in the design process for multifunctional chelators.

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Structure-property relationships in an ambipolar organic semiconductor cum NLO material: New insights from energy frameworks and charge density analysis

P. Munshi,1 K. K. Jha,1 S. B. Srivastava,2 D. Chakraborty,2 P. Johari,2 S. P. Singh2

1Department of Chemistry, 2Department of Physics, School of Natural Sciences, Shiv Nadar University, Dadri, UP 201314, India – parthapratim.munshi@snu.edu.in

Keywords: Charge Density Analysis, Energy Frameworks, Organic Semiconductor, Nonlinear Optical Materials.

Fundamental understanding of structure-property relationships in organic functional materials has been a prime focus of the materials researchers, in recent times. Importance of the relationships between the structure-property and charge carrier mobility has also been addressed. Exploration of charge-transfer phenomenon in organic molecular systems has received a great attention too. Here we report a small organic molecule, trans-4-nitro-4'-dimethylamino-α-cyanostilbene (NNDM-CNS), which exhibits high yet balanced ambipolar charge carrier mobility (hole: 6.7 cm²/Vs; electron: 1.7 cm²/Vs) in its single-crystal form and promising nonlinear optical (NLO) activity in its powder form. This is one of the rarest examples of small organic materials with such dual characteristics. Hole and electron mobility are determined based on space charge limited current (SCLC) technique on its pure single-crystal based diodes (Figure 1a). NLO properties are estimated using gas-phase (microscopic) and periodic (macroscopic) theoretical calculations on its crystal geometry. These important properties are correlated with its structure upon spectroscopic and high-resolution based structural studies and energy framework analysis followed by experimental charge density analysis. The later advanced approaches provide new insights to the structure-property relationships study in organic semiconductor. Quantitative and qualitative analyses of interaction energies (Figure 2) and electron densities (Figure 1b and 1c) clearly demonstrate that charge transport in organic crystals is purely governed by its molecular packing, especially the π-π stacking geometry. While the balanced ambipolar charge transport behavior makes this highly stable and highly soluble organic material promising for applications in optoelectronic devices, the encouraging values of NLO properties claim its potentiality as an NLO material. Moreover, this report introduces the crucial role of energy frameworks and charge density analysis for better understanding of structure-property relationships in organic semiconductors.
**Fig. 1** (a) Semiconductor diode device based on NNDM-CNS single-crystal. Electrostatic potential map, highlighting the $\pi$-**$\pi$** interactions, is drawn at the interval of ± 0.1 eÅ$^{-3}$ (b) 3D static deformation density maps. The intramolecular C-H...N interaction is shown in dotted line. The positive (blue surfaces) and negative (red surfaces) contours are starting at ±0.05 e Å$^{-3}$ and with an interval of ±0.1 e Å$^{-3}$. (c) Intermolecular C-**$\pi$**C-**$\pi$** interactions shown via BPs (golden lines), BCPs (red dots) and RCPs (yellow dots) along with the concerned atom labels.

**Fig. 2** CrystalExplorer based (a) energy frameworks with 100 energy scale factor and zero energy threshold, viewed down the $b$-axis and (b) interaction energies, showing the major contributions due to $\pi$-$\pi$ stacking interactions.

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**References**

Revisiting the structure of “Pbca” (±)[Co(en)₃]I₃.H₂O – comparing the results obtained by X-ray and neutron diffraction with those predicted with PLATON and the Flack test when using X-ray data alone

Ivan Bernal,¹,² Khurshid Sohail,¹ Roger A. Lalancette,¹ Alison Edwards³

¹Department of Chemistry, Rutgers University, 73 Warren Street, Newark, N. J. 07102, USA
²Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, 2050 Johannesburg ZA
³Australian Centre for Neutron Scattering

We became interested in the existing literature for the crystallization behavior of (±)-[Co(en)₃]I₃.H₂O and the absolute configuration of its enantiomers because of our project on the historical sequence of chemical studies leading Werner to formulate his Theory of Coordination Chemistry. In the process of so doing, we discovered a number of interesting facts, including the possibility that the published “Pbca” structure of the (±)-[Co(en)₃]I₃.H₂O was incorrect, and that it really crystallizes as a kryptoracemate in space group P₂₁2₁2₁. Other equally interesting facts concerning the crystallization behavior of [Co(en)₃]I₃.H₂O are detailed, together with an explanation why, in this, as in other cases in print, both the Flack parameter and PLATON, incorrectly, select the space group Pbca instead of the correct choice, P₂₁2₁2₁.
The many faces of localization-delocalization matrices

Ronald L. Cook

Molecular Design Innovations, Lakewood Colorado, USA –303-985-5497, mldcook@gmail.com

Keywords: LDM, electron pair densities, Principal Components, CSI, GINI

One of the ongoing limitations of model building in chemistry is the need for a domain expert to select the features (descriptors) that algorithms can transform into models of properties and activities. While these approaches have been quite successful, for example in pharmaceutical applications, their success may be due to the fact that a major part of the complexity that the trained models capture is due to the high level of information and complexity that are engineered into the descriptors employed for training the models.

Aware of the various limitations of current algorithms and the need for high quality domain expertise, some workers in the field of Machine Learning have started to ask if the underlying data complexity and potential hidden relationships can be more efficiently dealt with by shifting attention from engineering descriptor complexity to engineering the architecture and training of the machine-learning systems. With the increasing power of computer hardware, the growing availability of cloud-based storage, and the development of new algorithms, Machine Learning (ML) methods classified as Deep Learning are increasingly being used discover new relationships.

Unfortunately, ML methods generally require large databases of structures and properties or structures. The synthesis and characterization of a large number of new materials is not trivial. Furthermore, the programming caution “Garbage in, Garbage out” applies as much to ML as it does to standard regression methods and their use of domain expert engineered descriptors. Leonardo da Vinci was a great observer of nature and admonishes us with the words “But since such masters (domain experts) are so rare that there are but few of them to be found, it is a surer way to go to natural objects, than to those which are imitated from nature with great deterioration (designed descriptors), and so form bad methods; for he who can go to the fountain does not go to the water-jar”. (bolded words inserted by the author). What Leonardo da Vinci means by this is that you should go to the source. So where do we go to find the source for inputs for ML algorithms to transform the information about known materials into models for materials discovery? The answer, the ground state electron density.

For all materials, Density Functional Theory (DFT) tells us that the ground state properties of a many-electron system are uniquely determined by its electron density. The electron densities define the Hamiltonian, which defines the wavefunction which in turn determines all the properties. The author, extending work started by Prof. Cherif Matta, has developed a new set of descriptors that uses the electron pair densities as inputs into ML algorithms. Although the electron pair densities embodied in Prof. Matta’s Localization-Delocalization Matrices are not the full electron densities posited to determine all of the properties of a material, the new electron pair density descriptors have worked well across a wide range of systems [1-3]

To build LDMs, we extract a two-dimensional topological matrix of electron pair densities from computed wavefunctions using Bader’s Atoms-in Molecules (AIM) methods as embodied in AIMALL™. In the AIM description of the electron pair density, the number of electrons localized to one atomic basin is called the Localization Index (DI) and the number of electrons delocalized...
between one atomic basin and every other basin in the molecule is called the delocalization index (DI). The full set of molecular LIs and DIs can be organized in a two-dimensional matrix called the Localization-Delocalization matrix (LDM). The LDM condenses a considerable amount of information about the electron distribution at an atomic resolution. The LDM also encodes implicitly for atomic charges. Because it is based on the electron pair densities, the LDM also encodes information on the bond-path, the molecular graph, bond strengths, molecular topology, atomic electron populations and the free valences (Matta, 2018).

From the output of AIMALL™, AIMLDM [5] is used to build the LDMs. There are several flavors (faces) of the electron pair density matrices. One (the LDM) includes Localization Indices (LI), the bonding Delocalization Indices (b-DI) and the nonbonding Delocalization Indices (nb-DI). Another which represents primarily the electronic effects, the Delocalization Matrix (DM), replaces the LI’s with zeros. The LDMs and DMs can themselves be used as a descriptor by computing the Frobenius distance. In more a generally applicable approach the use of matrix invariant techniques can be used to extract eigenvalues from the LDM and DM matrices for use in building good cross validated models. We will present a sampling of some of the faces of the LDM and the DM and their correlation to physical properties and their use in model building

Acknowledgments

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References

Use of differential electron density to elucidate the origins of stereoselectivity in synthetic organic reactions

Paul Ha-Yeon Cheong,¹ H. Camille Richardson,¹ Alex C. Brueckner,¹ Daniel Walden,¹
Ronald L. Cook²

¹ 153 Gilbar Hall, Department of Chemistry, Oregon State University, Corvallis, OR 97330, cheongh@oregonstate.edu
² Molecular Design Innovations, Lakewood Colorado, USA –303-985-5497, mldcook@gmail.com

Keywords: LDM, electron pair densities, DFT, stereoselectivity, catalysis

Quantum mechanical computations have been used for decades to explain the origins of catalysis and selectivity in a variety of synthetic transformations.[1] In the majority of these cases, explanations of the origins of catalysis and/or selectivity are made based on chemical intuition, model systems, or indirect methods such as the NBO analyses[2] or distortion/interaction models.[3] Herein, we provide a way to identify these factors directly from the computations, thereby providing an unambiguous and unbiased relationship between the quantum mechanical wavefunction and the observed trends. We demonstrate the use of quantum mechanics (density functional theory), Quantum Theory of Atoms in Molecules (QTAIM),[4] "localization-delocalization matrices" (LDMs),[5] dimensionality reduction, and statistical regression towards the identification of the origins of stereoselectivity in synthetic organic reactions.[6] To be specific, the atomic electron density differences between diastereomeric transition states were correlated to the differences in energies. Ultimately, this gives an exact atomic representation of which nuclei are responsible for the selectivity in a given reaction. This has been demonstrated for reactions catalyzed by small organic molecules (organocatalysis) studied in our group. Visual representations of the atoms responsible for the selectivities in the transition states will be revealed.

Acknowledgements

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[5] "AIMLDM: A Program to Generate and Analyze Electron Localization-Delocalization Matrices (LDMs),"

Half-metallicity of graphite-like and amorphous carbon nanoparticles and their potential applications in spin catalysis: Quantum chemistry predictions

Gilles H. Peslherbe,1,2 Oleksiy Khavryuchenko2,3

1 Department of Chemistry and Biochemistry, Concordia University, Montreal, Canada – gilles.peslherbe@concordia.ca
2 Centre for Research in Molecular Modeling, Montreal, Canada
3 Research and Development Department, TMM LLC, Kyiv, Ukraine – alexkhavr@gmail.com

Keywords: carbon nanoparticles, half-metallicity, spin catalysis, electronic structure calculations

Model carbon nanoparticles representative of the graphite-like and amorphous domains of active carbon were investigated with computational quantum chemistry, namely density-functional theory (DFT) [1] and the very high-level complete active space self-consistent field (CASSCF) method [2]. Both types of nano-sized clusters are found to be half-metallic, i.e. various spin states have equal or similar stability. The model carbon clusters are found to possess a multi-configurational electronic structure dominated by high-spin configurations, and characterized by the presence of antiferromagnetically coupled electron pairs. The concept of catalysis over such spin-conductive mediators was further investigated. Specifically, homolytic C-C bond cleavage in ethane over small half-metallic carbon clusters in the presence of a methyl radical was considered as a paradigm [3]. The methyl radical (spin catalyst) and carbon cluster (mediator) are found to share a common electronic orbital containing the radical unpaired electron, allowing nascent radicals emerging from ethane dissociation to interact with the spin catalyst through the carbon electronic system. This could make spin flip possible, affording formation of a triplet radical pair not prone to recombination, and would thus result in the acceleration of the reaction rate. Nanoparticles may thus find new applications in controlled catalytic processes by allowing normally spin-forbidden reactions and not necessarily lowering activation barriers in the traditional sense of chemical catalysis.

Fig. 1 Spin density distribution of the broken-symmetry singlet and the multiplicity 9 state of a model carbon nanoparticle. Also shown is a schematic depiction of the spin flip of the electrons in weakly overlapping singly-occupied orbitals that converts the singlet state into the multiplicity 9 state [Taken from Ref. 1].
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References

Poster Presentations
Alphabetical Order by Author
On the thermodynamic stability and the natural selection of canonical nucleosides in the prebiotic evolution of life

Lázaro A. Monteserín Castanedo,1-3 Chérif F. Matta2, 3

1 Faculty of Biology, University of Havana, Cuba – lamonteserincastanedo@gmail.com
2 Dept. of Chemistry & Physics, Mount Saint Vincent University, Halifax, NS, B3M 2J6, Canada – cherif.matta@msvu.ca
3 Dept. of Chemistry, Saint Mary’s University, Halifax, NS, B3H 3C3, Canada – cherif.matta@msvu.ca

Keywords: molecular evolution, prebiotic chemistry, nucleic acid stability

How did nature select the building blocks of life [1-6]? The choices are quasi-infinite, so why those molecules in particular and not any of the myriads of others? These are way too ambitious problems to tackle in one generation let alone by one research group. Instead, a set of infinitely more modest questions in this general area is being addressed in this work. The question addressed in the present poster can be posed as: Has thermodynamics played a decisive role in the evolutionary selection of one of two possible isomers of present day nucleic acids? More specifically, all known DNA and RNA nucleosides found in nature have an α-configuration at the C2' carbon of the sugar as opposed to a β-configuration (Fig. 1). Simple molecular modeling demonstrates that, at least geometrically, one can in fact create a “wrong” α-DNA with equal ease as to the common β-type (Fig. 2).

PM7 semiempirical method was used to estimate the relative stabilities of thousands of randomly-generated rotational conformers of both the α- and β-configurations in vacuum, and in solvents including water and formamide (believed to have dominated in certain geologic times). These calculations were performed within the Multiple Minimum Hypersurface (MMH) approach [7] for an exhaustive exploration of the potential energy hypersurface whereby 1000 different conformations were generated for every configuration in every solvent studied. Thermodynamic properties were then calculated from a subsequent standard statistical mechanical treatment. The most stable conformations obtained at the semiempirical level were then re-optimized at the density functional theory (DFT) level using a 6-31G(d,p) basis set in conjunction with the B3LYP and M06-2X functionals. Preliminary data suggest that β-ribonucleosides appear to be universally more stable thermodynamically than their α-counterparts under all studied solvation

Fig. 1 (Left) An α-DNA nucleoside (adenosine, dA), which is never observed in present day nucleic acids. (Right) The β-isomer of dA which exists in present day nucleic acids.
conditions. It thus plausible that a slight thermodynamic advantage drove evolution to select the observed present-day β-nucleic acids.

![Diagram of DNA structures](image_url)

**Fig. 2 (Top)** Natural configuration of present day DNA double-helical structure in Watson-Crick pairing mode. **(Bottom)** A molecular model that demonstrates the possibility of having perfectly good Watson-Crick base pairing in the “wrong/non-natural” α-DNA.

**Acknowledgements**

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**References**

A “direct” mechanism for the action of the genoprotectors extracted from the Cuban plant *Phyllanthus orbicularis* K

Lázaro A. Monteserín Castanedo,1,3 A. S. Lamar,1 C. M. Boado,1 A. d.l. Nuez-Veulens,4 R. Rodríguez Fernández,5 Chérif F. Matta2,3

1 Faculty of Biology, University of Havana, Cuba – lamonteserincastanedo@gmail.com
2 Dept. of Chemistry & Physics, Mount Saint Vincent University, Halifax, NS, B3M 2J6, Canada
3 Dept. of Chemistry, Saint Mary’s University, Halifax, NS, B3H 3C3, Canada
4 Faculty of Chemistry, University of Havana, Cuba
5 Dept. of Computational Medicine, Institute of Nephrology, “Abelardo Bush López”, Cuba

**Keywords:** genoprotecting natural phenols, carcinogenic amines, computational phytochemistry

Several degenerative diseases are at least partly caused by damage to the genetic material (i.e. through genotoxicity) brought about by genotoxic agents such as aromatic amines [1]. Aqueous extracts of *Phyllanthus orbicularis* K (PoK), a plant indigenous to Cuba, has been found to reduce the genotoxicity of aromatic amines such as meta-fenilendiamine (m-PDA), 4-aminobiphenyl (4-ABP), and 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) [1,2]. These carcinogenic amines are ubiquitous in our environment and are found in cooked meat and fish (0.6 to 50 ng/g of meat) and are believed to form DNA adducts leading to several cancers [3]. This genoprotective action has been attributed to the presence, in the PoK extract, of phenolic compounds such as 2,4 di-terbutylphenol (DTBP) and its dimer 2,6 di-secbutylphenol (DSBP), however, the molecular mechanism of this action is unknown and is a subject of this work [4]. Thousands of conformers of each possible phenol/protectant-amine/carcinogen pairs were studied in both vacuum and in aqueous medium with the Multiple Minimum Hypersurface methodology (MMH) [5] at the PM7 semiempirical level of theory. The geometries and energies of the lowest energy complexes were then refined with density functional theory (M05-2X/6-31G(d,p)) calculations. Since the studied complexes were found to be thermodynamically stable, it is postulated that the genoprotective effect is the result of the direct complexation/pairing of the protective phenol with the genotoxic amines inhibiting its binding to its critical target biopolymers [4]. A post-electronic structure QTAIM study unraveled the non-classical chemical interactions that accompany the stability of the protectant-carcinogen complexes [4].
Fig. 1 An example of a stable protectant (phenol) – carcinogen (amine) complex stabilized by several weak bonding interactions revealed in the electron density molecular graph (left) as well as in the reduced density gradient NCI plot (right). (The protectant is the monomer at the top of the figure and the carcinogenic amine the one at the bottom.

Acknowledgements

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References

Interpretation of the Kernel Energy Method (KEM) using the theory of Interacting Quantum Atoms (IQAs)

Youji Cheng,¹,² Todd A. Keith,³ Lou Massa,⁴ Chérif F. Matta¹,²

¹ Dept. of Chemistry & Physics, Mount Saint Vincent University, Halifax, NS, B3M 2J6, Canada
² Dept. of Chemistry, Saint Mary’s University, Halifax, NS, B3H 3C3, Canada
³ SemiChem, Inc., Shawnee, KS 66216, USA
⁴ Hunter College and the Graduate School, City University of New York, New York, NY 10065, USA

Keywords: KEM, IQA, fragmentation quantum mechanical approaches, reconstruction of macromolecules

The Kernel Energy Method (KEM) of Massa, Huang, and Karle [1-12] is a many-body expansion method of predicting the energy and other quantum properties of large molecules from fragments thereof, called kernels. In this poster, atomic energies and their intra-atomic and inter-atomic contributions as defined by QTAIM and the Interacting Quantum Atoms method (IQA) and are used to provide a detailed physical understanding of KEM.

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References

IP data correction for accurate charge density study

Yuka Deguchi,¹ Eiji Nishibori,¹,² Bo Iversen³

¹ Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan – s1720270@s.tsukuba.ac.jp
² Faculty of Pure and Applied Sciences, University of Tsukuba, Japan – nishibori.eiji.ga@u.tsukuba.ac.jp
³ Department of Chemistry & Center for Materials Crystallography, Aarhus University, Denmark – bo@chem.au.dk

Keywords: Data correction, Imaging plate, Charge Density Study, Diamond

We have reported the synchrotron powder diffraction data of diamond at 300K with, sinθ/λ = 2.22 Å⁻¹ and 800 K with 2.11 Å⁻¹ resolution [1]. The intensities of Bragg reflection in more than 2.0 Å⁻¹ resolution of 800 K were approximately half of those of 300 K. We measured the new datasets to use higher resolution data at 800K for charge density study.

Synchrotron radiation (SR) powder diffraction experiment was carried out at SPring-8, BL02B2. A Large-Debye Sherrer camera with an imaging plate (IP) as a detector was used in the measurement [2]. We can ignore the oblique incidence effect using the curved IP system. We used the BAS-MS IP and Fuji BAS 2500 IP scanner. We measured three two-dimensional (2D) powder data. Exposure time were 20, 80 and 320 minutes. The IP was read more than 20 minutes after X-ray exposure to avoid the fading effect. The following parameters were used in reading: 50 μm×50 μm pixel size, 16 Gradation, Sensitivity 1000 and Latitude 4. Two sets of one-dimensional (1D) powder data were prepared from one 2D powder data. One of the data was prepared by the integration with 51 pixels in the perpendicular direction of 2θ. Another data was prepared by the integration with 401 pixels to improve counting statistics in the higher angle regions.

We estimated the noise of six powder profiles. We call the profiles 1st, 2nd, 3rd, 4th, 5th and 6th data. Table 1 shows the noise of background for 300K. Where \( I_{\text{back}} \) is the counts of background, \( \sigma_{\text{obs}} \) is the noise, \( \sigma_{\text{sta}} \) is the \( 2/\sqrt{I_{\text{back}}} \). Figure 1 shows the plots of the ratio between noise and intensity. We found \( \sigma_{\text{obs}} \) in 6th data is three times larger than \( \sigma_{\text{sta}} \). This noise of the data consists of the counting statistical error and the detector noise.

We observed periodic intensity modulation in 6th data. We found that it derived from the discrepancies of the reflectivity for six-sided polygon mirror of the IP reader. The fluctuation is less than 1%. Figure 2 shows the powder profiles of 6th data. The purple is the uncorrected data. We can recognize periodic intensity drops in the data. The green is the corrected data. We multiply periodic correction factors to the data. The maximum value of the correction factors is 1.003. The noise decreased by 40% in the corrected data. We performed Rietveld refinement using corrected datasets. Reliability factors based on integrated intensities was 2.35% that was 0.44% better than before correction. We are doing analysis for 800 K datasets.
**Table 1** The noise of background for six powder profiles of 300K data

<table>
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<th>Profile</th>
<th>Exposure Time [min]</th>
<th>Integration Width [pixel]</th>
<th>$\sigma_{\text{back}}$</th>
<th>$\sigma_{\text{obs}}$</th>
<th>$\sigma_{\text{sta}}$</th>
<th>$\sigma_{\text{obs}}/\sigma_{\text{sta}}$</th>
<th>$\sigma_{\text{obs}}/\sigma_{\text{back}}$</th>
<th>$\sigma_{\text{sta}}/\sigma_{\text{back}}$</th>
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<tr>
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<td>1.3%</td>
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<tr>
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<td>80</td>
<td>51</td>
<td>20000</td>
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<td>280</td>
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<td>1.4%</td>
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<tr>
<td>4th</td>
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<tr>
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<td>401</td>
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<td>1600</td>
<td>3.21</td>
<td>0.81%</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

**Fig. 1** The plots of the ratio between noise and intensity for $\sigma_{\text{obs}}$ (closed square) and $\sigma_{\text{sta}}$ (open triangle).
Acknowledgements

The synchrotron experiments were performed at SPring-8 BL02B2 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) as a Partner User (Proposal No. 2017A0074). This work was also supported by JSPS KAKENHI Grant Numbers JP17H05328 and JP16K13660, the JSPS Bilateral Open Partnership Joint Research Projects for 2015−2017 and 2017−2019, the International Education and Research Laboratory Program of Univ. of Tsukuba. This work was also partly supported by SEI group CSR foundation and CASIO SCIENCE PROMOTION FOUNDATION.

References

Theoretical study of electron density and energy transfer in photophysical processes

Jesús Hernández-Trujillo, Jesús Jara-Cortés, Jorge Peón-Peralta, Edith Leal-Sánchez

1 Facultad de Química, UNAM, Ciudad de México, México – jesusht@unam.mx
2 Facultad de Química, UNAM, Ciudad de México, México – josejc@comunidad.unam.mx
3 Instituto de Química, UNAM, Ciudad de México, México – jpeon@unam.mx
4 Facultad de Química, UNAM, Ciudad de México, México – edithleal290896@live.com

Keywords: excited states, charge and energy transfer, excimers, conical intersections, electron density

The information carried by the electron distribution on the mechanisms of photophysical processes is presented for selected systems involving excimer formation, avoided crossing of electronic states or conical intersections. The charge and electronic transfer are analyzed for intra- and intermolecular interactions using the quantum theory of atoms in molecules and the interacting quantum atoms approach. As examples, the formation of rare gas and aromatic excimers, the deactivation of uracil (see Figure 1) and nicotinamide related compounds from their brilliant excited states are discussed. The effect of electronic excitation on the molecular stability and the rationalization of emission spectra of molecules of biological interest are discussed in terms of real-space properties of the charge density.

Figure 1. a) Minimum energy paths (in eV) for the lowest singlet electronic states of uracil b) Electron density difference envelopes (Δρ =0.005) between the excited and ground states and main changes in the atomic charges upon excitation, and c) Changes in the interacting quantum atoms energy components for the $S_0 \rightarrow ^1\pi\pi$ transition. In b), red and blue envelopes denote electron density decrease and increase, respectively.
Acknowledgements

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References

Determination of spin and orbital moments in Nd$_2$Ir$_2$O$_7$ using magnetic Compton scattering

Daniel O’Neill,$^1$ Jon Duffy,$^1$ Stephen Dugdale,$^2$ Sean Giblin,$^3$ Jon Taylor$^4$

$^1$Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom – D.O-Neill.1@warwick.ac.uk
$^2$School of Physics and Astronomy, Cardiff University, Cardiff CF24 3AA, United Kingdom
$^3$H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom
$^4$DMSC–European Spallation Source, Universitetsparken 1, Copenhagen 2100, Denmark

**Keywords:** Compton Scattering, Spin Densities, Spin orbit coupling, Iridates

Nd$_2$Ir$_2$O$_7$ has recently gathered interest both from its pyrochlore structure, which can lead to frustration and novel transport properties such as a Metal to Insulator Transition (MIT) [1], and the interplay of spin orbit coupling and the electron-electron interactions often found in 5d transition metal oxides [2]. It’s this interplay that can be investigated by comparing the spin and orbit contributions to the total moment for the neodymium and iridium separately at temperatures through and around the reported MIT, the exact temperature of the MIT appears to be sample dependant but is generally agreed to be 33K [2].

In this study we used the Magnetic Compton Scattering technique to investigate the spin moment of Nd$_2$Ir$_2$O$_7$. Using Magnetic Compton Scattering experiments, it is possible to directly obtain a 1D projection of the spin polarised electron density distribution, along the scattering vector [3]. This can be integrated to measure the bulk spin moment of the material. Comparing this moment to bulk total measurements, measured using, for example, a SQUID, it is possible to also calculate the bulk orbital moment of the material [4].

This was performed on Nd$_2$Ir$_2$O$_7$ at a range of temperatures between 2K and 60K. The spin and orbital moments were also separated out to their neodymium and iridium components to observe any changes through the MIT. We found the neodymium 4f spin and orbital moments both decrease with temperature leaving a 5d like moment that stays constant over this temperature range. We measured two samples and whilst we found the values of the moments differed this temperature dependence was consistent between the two.

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**References**

Total X-ray wavefunction refinement

Rumpa Pal,¹ Emanuel Hupf,¹ Lorraine A. Malaspina,¹ Dylan Jayatilaka,² Simon Grabowsky¹

¹ University of Bremen, Department 2: Biology/Chemistry, Bremen, Germany – rpal@uni-bremen.de
² University of Western Australia, School of Molecular Sciences, Crawley, Australia – dylan.jayatilaka@uwa.edu.au

Keywords: quantum crystallography, X-ray structure refinement, quantum chemical molecular electron density, H atom modelling, anisotropic displacement parameters

Hirshfeld atom refinement (HAR) [1] is a structural refinement method for single-crystal X-ray diffraction data that uses an aspherical atom partitioning of tailor-made ab initio quantum mechanical molecular electron densities, in contrast to spherical scattering factors used in the Independent Atom Model (IAM). The original HAR has been extended by implementing an iterative procedure of successive cycles of electron density calculations, Hirshfeld atom scattering factor calculations and structural least-squares refinements, repeated until convergence.

X-ray constrained wavefunction (XCW) [2] fitting as a separate technique overcomes the shortcomings of the theoretical ansatz used by including experimental observations (such as electron correlation or the crystal effect) into the wavefunction.

In X-ray wavefunction refinement (XWR) [3,4], HAR is followed by an adjustment of the electronic wave function through XCW fitting. Similar to the implementation of an iterative procedure within HAR itself, a natural forward step of sophistication for XWR would be to directly incorporate the fitted wavefunction into a new HAR, obtain an improved geometry and improved displacement parameters and use this as input for another XCW fitting, and so on, until convergence in both energy and geometry: Total XWR = HAR + XCW + HAR + XCW + …

In this study we have introduced the above sequence by benchmarking against experimental and theoretical results on the well-studied systems urea and L-alanine. At first, we investigate the magnitude of the effects of electron correlation and polarization (via the crystal effect) on the electron density as they are introduced from the structure factors into the wavefunction through a simple XCW fitting. Second, we study to which extent the geometrical results and the atomic displacement parameters improve relative to a simple HAR if the fitted wavefunction is used in a total XWR. Third, we study to which extent the information extracted from the structure factors and incorporated into the wavefunction (electron correlation and polarization) are enhanced relative to a simple XCW fitting (see Figure 1).

We will furthermore present applications of the total XWR procedure to rare and subtle chemical features, such as the presence of a non-nuclear attractor in a stable molecular species, the dimeric Mg(I) molecule [5] and resonance in an organolithium complex, 2-Picolyllithium (PicLi) [6].
Fig. 1 Difference density (isovalues = ±0.005 a.u.), A. Original XWR, $\Sigma \rho(\lambda=0.044) - \Sigma \rho(0.0) = 0.383e$
B. Total XWR, $\Sigma \rho$(Total XWR) - $\Sigma \rho$(Original XWR) = 0.123e.

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References

Experimentally refined density functional theory on strongly correlated materials

Ding Peng, 1 Andrew E. Smith, 2 Philip N. H. Nakashima 3

1 Dept. of Materials Science & Engineering, Monash University, Victoria 3800, Australia – ding.peng@monash.edu
2 School of Physics and Astronomy, Monash University, Victoria 3800, Australia – andrew.e.smith@monash.edu
3 Dept. of Materials Science & Engineering, Monash University, Victoria 3800, Australia – philip.nakashima@monash.edu

Keywords: Density functional theory, Quantitative convergent-beam electron diffraction, Strongly correlated electron systems

Quantitative convergent-beam electron diffraction (QCBED) is regarded as one of the most accurate and precise experimental techniques for measuring bonding charge density-sensitive structure factors [1,2]. Density functional theory (DFT) is ubiquitous in materials science as a theoretical method for making predictions of materials properties based on its ab-initio calculations of electron density within crystalline materials. The Fourier coefficients that can be used to specify this electron distribution are structure factors that can be used in diffraction calculations such as those employed by QCBED in the process of pattern matching a calculated diffraction pattern to an experimental one. This means that an experimental technique like QCBED can readily be hybridised with DFT and may provide means by which specific parameters within the DFT model can be refined by experiments. This approach of using experimental constraints in determining theoretical wave functions is not new and unique to this work [3], however the present approach of combining QCBED with DFT is. This hybridisation is illustrated in figure 1.

The flow chart of our developed program, shown in figure 1, demonstrates the intersection of QCBED and DFT+U [4]. The latter is known to be an efficient DFT approximation to the electronic structure of strongly correlated materials, a category of materials which has traditionally been problematic to model. The Hubbard energy term, U, which describes the Coulomb interaction of localized electrons, is refined in this scenario. The structure factors generated by DFT+U are substituted into the Bloch-wave formalism for calculating electron diffraction patterns. The theoretically calculated CBED patterns are then pattern matched with the experimental ones to refine parameters of the DFT calculation. We demonstrate the approach for NiO, which is a well-known strongly correlated electron system. Figure 2 illustrates the sensitivity of our QCBED/DFT+U hybridisation to the Hubbard term, U, in this material.
Fig. 1 The flow chart illustrating the hybridisation of QCBED with DFT and the manner by which that latter is structurally incorporated into the former.
Fig. 2 Comparison of CBED patterns of NiO near [110] zone axis incidence simulated with Hubbard term U=0eV in (a) and U=6eV in (b). The difference map in (c) is obtained by subtracting the intensities in pattern (b) from pattern (a). (d) illustrates the geometry of the CBED patterns in (a) and (b) as well as indices of the reflections included in the simulation. The red cross in (d) indicates the location of the [110] zone axis, which is exactly at the centre of the 4 indexed reflections.

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References

The Chemistry of transition metal structure

Malavikha Rajivmoorthy, Tim Wilson, Mark E. Eberhart

Molecular Theory Group, Colorado School of Mines, USA – mrajivmoorthy@mines.edu

Keywords: Transition metal structure, Relative critical sets, Quantum Theory of Atoms in Molecules (QTAIM)

We believe that developments in theoretical chemistry [1-5] may be applied to metallurgy and successfully implemented in the design of metals and alloys. As a preliminary step along this path, we seek relationships between transition metals crystallography (fcc, hcp, bcc) and the electronic charge density, which we will classify in term of its topological and geometric properties according to the Quantum Theory of Atoms in Molecules (QTAIM). Such an approach is ideally suited to the study of transition metal crystallography, as for the bcc, fcc, and hcp crystals the Wigner Seitz cell (Figure 1) is identical to the Bader atom and hence is energetically well-defined [6]. In addition to the Wigner-Seitz cell, it is also possible to construct similar energetically well-defined space filling polyhedra around different types of critical points, like the cage critical point where the charge density is a local minimum [7]. Here we refer to these cage centered polyhedral as electronic basins. As with all energetically well-defined polyhedra (those characterized by a zero flux surface in the gradient of the charge density) the virial theorem is satisfied and hence electronic basins of highest average kinetic energy will be preferred. To achieve this high value, charge density redistribution occurs from cages (of high potential) where atoms are locally least densely packed and the Laplacian is most positive to cages of low potential and smaller Laplacian. In transition metals, this charge transfer proceeds through a loss of density from octahedrally coordinated cages and an accumulation of density in tetrahedral coordinations. As an example we will explore the charge transfer accompanying the fcc to bcc transition of iron along the Bain path.

Fig. 1 Wigner Seitz cells of (a) early hcp, (b) bcc, (c) late hcp, and (d) fcc transition metals from the first row. The points indicate critical points, and the lines indicate bond paths.

References

Electron density redistribution during a photoinduced geometrical change of copper (I) complexes

David Ramírez-Palma,¹ Luis Gutiérrez-Arzaluz,² Lillian Ramírez-Palma,³ J. Peón,⁴ Fernando Cortés-Guzmán⁵

¹ Institute of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico – david.ramp49@gmail.com
² Institute of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico – luis.gtz.arzlz@gmail.com
³ Institute of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico – lila.gis.rp@gmail.com
⁴ Institute of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico – jpeon@unam.mx
⁵ Institute of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico – fercor@unam.mx

Keywords: Quantum Chemical Topology, Copper (I) complexes, metal-to-ligand charge transfer, excited states.

The photochemical and photophysical properties of bisdiimine copper (I) complexes have been of interest for many years due to the photoinduced structural change that comes together with a charge transfer from metallic center to ligands [1]. Most experimentally studied system is bis(1,10-phenanthroline) copper (I) complex. The complex with a $D_{2d}$ geometry at ground state ($S_0$) changes to an almost plane base upon excitation, because of the copper (I) oxidation [2,3]. However, in the excited state, charge transfer is reversible and partial, and involves more than just one excited state. In the complete suggested process, complex is excited to $S_1$ state, where geometry relaxation takes place until reach the minimum in the PES. At this point, a deactivation to $S_0$, $T_2$ or $T_1$ states can occur [4,5]. The topological properties of electron density and of its laplacian were studied in order to understand the changes involved in the metallic center and ligands upon photoexcitation process. This kind of information could be useful in the design of new systems to control molecular motion with different light sources.

Atomic graphs for electronic states involved in excitation process of copper (I) complex.

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References

Theoretical study of reactions mediated by ternary Cu(II) complexes

L. G. Ramírez-Palma,1 J. C. García-Ramos,1 L. Ruiz-Azuara,2 F. Cortés-Guzmán1

1 Institute of Chemistry, National Autonomous University of Mexico, Department of Physical Chemistry, Mexico City, Mexico – lila.gis.rp@gmail.com, jcgarcia@comunidad.unam.mx, fercor@unam.mx
2 Faculty of Chemistry, National Autonomous University of Mexico, Department of Inorganic and Nuclear Chemistry, Mexico City, Mexico – lenar701@gmail.com

Keywords: Casiopeinas, cancer, disulfur bond, reactive oxygen species, QTAIM.

Casiopeinas® is the name of a copper (II) complexes family that had been studied in vitro and in vivo, showing genotoxicity, cytotoxicity and antineoplastic activity [1,2]. The mechanism of action for these complexes is not well understood yet. Nevertheless, experimental and theoretical results suggest that the antineoplastic activity is consequence of: (a) the redox capacity of Cu (II), to generate reactive oxygen species (ROS) that produce cytotoxicity [3], and (b) to a direct interaction with the DNA by intercalation in the minor groove [4]. These complexes catalyze the disulfur bond formation reaction in thiolated systems, by an electron transfer mechanism (see figure 1). The aim of this work is the study of the reactions involved in the molecular recognition of Casiopeinas®, by DFT calculations and the analysis of electron density properties, helping to understand the mechanism of interaction with DNA for these compounds.

Fig. 1 Proposed mechanism for the electron transfer involved in the disulfur bond formation.
Acknowledgements

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References

Pinpointing origins of selectivity with dimensionally reduced electron density

H. Camille Richardson, 1 Alex C. Brueckner, 1 Daniel M. Walden, 1 Ronald L. Cook, 2 Paul Ha-Yeon Cheong 1

1 153 Gilbert Hall, Department of Chemistry, Oregon State University, Corvallis, OR 97330, cheongh@oregonstate.edu
2 Molecular Design Innovations, Lakewood Colorado, USA –303-985-5497, mlcook@gmail.com

Keywords: LDM, electron pair densities, DFT, stereoselectivity, catalysis

While quantum mechanical (QM) computations have been used for decades to explain the origins of selectivity in a variety of synthetic transformations,[1] explanations of the origins of catalysis and/or selectivity are usually made based on chemical intuition, model systems, or indirect methods,[2,3] rather than any form of direct analysis. In this work we detail a method of identifying the features that lead to selectivity directly from computations, providing a specific and easily identifiable relationship between the QM wavefunction and observable trends. A combination of density functional theory, Quantum Theory of Atoms in Molecules (QTAIM),[4] "localization-delocalization matrices" (LDMs),[5] dimensionality reduction techniques, and statistical regression, leads to a direct relationship between observed selectivities and their origins.[6] This is achieved through a correlation between differences in electron densities in diastereomeric transition states and the differences in their relative energies, which gives an atomic representation of the nuclei affected by changes in diastereomers. These changes relate directly to the selectivity in a given reaction. This has been demonstrated for several reactions catalyzed by small organic molecules studied in our group.

Acknowledgements

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References

X-ray charge density study of molybdenum

Tomoaki Sasaki,¹ Hidetaka Kasai,¹² Eiji Nishibori¹²

¹ Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan – s1630070@u.tsukuba.ac.jp
² Faculty of Pure and Applied Sciences and Tsukuba Research Center for Energy Materials Science (TREMS), University of Tsukuba, Tsukuba, Japan – nishibori.eiji.ga@u.tsukuba.ac.jp

Keywords: charge density, molybdenum, X-ray diffraction

Charge density of metals has attracted attention due to correlations with mechanical properties such as shear strength [1], Cauchy pressure [2], and Young's coefficients [3]. It is difficult to measure high resolution data of metal for charge density study. For example, Debye temperature of most metals is less than 500 K. An effect of thermal vibration due to the low Debye temperature requires low temperature measurement.

Molybdenum is a 5d transition metal. The crystal structure is bcc. The Mohs hardness of molybdenum is more than twice that of aluminum. Debye temperature of molybdenum is almost same as that of aluminum. The energy of K absorption edge of molybdenum is 20 keV. The fluorescence scattering intensity is relatively high if we use high energy X-ray which exceed to 20 keV.

Figure 1A shows synchrotron radiation powder data of molybdenum at room temperature. The data were measured at SPring-8, BL02B2 beamline. Horizontal line is diffraction angle 2θ and vertical line is intensity. The low intensity regions were expanded in these figures. The wavelength of incident X-ray is 37.7 keV. The data were measure from 0 to 108° in 2θ which corresponds to d > 0.204 Å in d-spacing range. An imaging plane was used as a detector. The peak intensities of 110 reflection of these data are approximately 1 000 000 counts.

We measured powder data using thin metal foils attached before the IP detector. Black line is the data without foil. Red line is the data using tantalum foil with 0.015 mm thickness. Purple line is the data using copper foil with 0.05 mm thickness and nickel foil with 0.05 thickness. The intensity of black line has no angular dependence. This fact indicates that this is mainly due to fluorescence scattering of molybdenum. A wavelength of fluorescence scattering is 17.4 keV. We used metal foils to remove the fluorescence.

Figure 1B, C and D shows expanded regions of the data as shown in Figure 1A. The fluorescence scattering were reduced in Figure 1C and D. The transmissions of 17.4 and 37.7 keV X-ray for the tantalum, the copper and the nickel foils are the same as 15 % and 75 %, respectively. Figure 1C shows intensity fluctuation in background. This is due to the fluorescence scattering of the tantalum foil. There are no such fluctuations in Figure 1D. We successfully removed fluorescence scattering of molybdenum sample and foils using a combination of copper and nickel foils.

We can recognize weak 880 reflection at 72.5° in Figure 1D. The measurement of weak reflection is crucial for high quality charge density study. The charge density study of low background and low temperature data are now on going.
Fig. 1 (A) Powder X-ray diffraction with no foil, tantalum foil, and copper and nickel foil. Powder X-ray diffraction data of $2\theta = 70$-76° with (B) no foil, (C) tantalum foil, and (D) copper and nickel foil.

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References

Computational investigation of polyhexamethylene biguanide (PHMB) mechanism of action on the bacterial membrane

Shahin Sowlati-Hashjin,¹ Mikko Karttunen,² Paola Carbone,³ Afroditi Zaki⁴

¹ University of Western Ontario, Department of Chemistry, London, Canada - shishjin@uwo.ca
² University of Western Ontario, Department of Chemistry, Department of Applied Mathematics, London, Canada -mkarttu@uwo.ca
³ University of Manchester, School of Chemical Engineering and Analytical Science, Manchester, UK - Paola.Carbone@manchester.ac.uk
⁴ University of Manchester, School of Chemical Engineering and Analytical Science, Manchester, UK

Keywords: PHMB, Bacterial Membrane

Cationic polymers such as polyhexamethylene biguanide (PHMB) have been of a great interest due to their high antibacterial activity and low toxicity to humans and have been employed as topical anti-infective solutions in ophthalmology, as disinfectants and biocides in water systems, in topical wound, on cotton and environments [1-3]. PHMB was commonly believed to kill bacteria by disrupting their membrane. In contrary, it has been recently proposed that PHMB enters cells and condenses bacterial chromosomes in a selective fashion [3]. In the present study, we have employed classical molecular dynamics and umbrella sampling methods to investigate the behavior of PHMB polymers and gram-negative membranes in order to shed lights on the potential PHMB mechanism of action on the bacterial membrane. Specifically, various properties (e.g., RMSD, area per lipid, and hydrogen bonding occupancies) of several systems including the membrane (made up with POPG and POPE with a 1:3 ratio), PHMB, PHMB-membrane (inserted and separated), were examined. Furthermore, membrane penetration by PHMB was examined using umbrella sampling approach. Our results suggest that a single PHMB molecule has a negligible structural effect on the membrane, while it can penetrate and pass through the membrane with a relatively low free energy barrier.

References

Gradient bundle analysis — Full volumetric charge density behavior in a single plot

Tim Wilson,1* Amanda Morgenstern,2* Mark Eberhart3*

1 Colorado School of Mines, Department of Chemistry, Golden, United States
twilson@mines.edu
2 amorgens@mines.edu
3 meberhar@mines.edu

Keywords: QTAIM, structure property relationships, DFT, gradient bundle analysis, chemical visualization

It is known from density functional theory that all information about a chemical system is contained in its electron charge density [1], but methods for extracting information about local properties exclusively from the charge density are in short supply. The quantum theory of atoms in molecules provides a language for the discussion of charge densities and a mathematical framework for their qualitative and quantitative comparison [2]. This perspective is unique in its agnosticism with regard to the type of systems under consideration—equally applicable to organic or metallic, molecular or solid-state, experimentally observed or purely theoretical—and has the potential to bridge distant fields of chemical and materials research. Building on this framework, gradient bundle analysis is a method for volumetric analysis of the charge density at arbitrary precision to extract local and global chemical properties [3-5]. By dividing an atomic basin into a large number of non-overlapping gradient bundles (see Fig. 1), each of which bounded by a zero flux surface in the charge density, one can associate the properties of interest in the bundles—e.g. electron count—with specific regions around the nuclear critical point by which the bundles were defined (see Fig. 2). This information can then be projected onto a sphere around the nuclear critical point, providing a powerful visualization tool; a method of reducing full volumetric information in the charge density to two dimensions. Here we introduce the method and present example applications.

Fig. 1 Some gradient bundles around the N atom in ammonia.
Fig. 1 Gradient bundle condensed electron count (around an O atom in water and a N atom in ammonia) showing lone electron pair regions.

References

Biographies
Miguel Álvarez Blanco (1969-2010):

Open letter to the participants of Sagamore 2018 on the occasion of the establishment of the Miguel Á. Blanco International Prize

Víctor Luaña Cabal

1 Departamento de Química Física y Analítica, c/ Julián Clavería 8, 33006-Oviedo, Spain
*Correspondence e-mail: vluana@uniovi.es; victor@carbono.quimica.uniovi.es

I was the PhD advisor of Miguel and I could enjoy meeting one of the brightest minds among those that our small group of researchers accumulates. If you ask how it is possible to have a group of intellectuals working together that means you never met the grandfather of our group: Lorenzo Pueyo, a most benign outstanding scientist himself.

I do believe that the relationship between PhD students and her/his advisors is (can be) a paternal-filial one. I certainly consider Lorenzo as my second father and Miguel a spiritual song. Surviving Miguel's passing was a tough test for me, even though having Miguel's widow at the door in front of my office at work has helped me to overcome the loss.

Miguel was a humble person by conviction and the best friend for his colleagues, always ready to help any person as much as he could. Calling Miguel brilliant only reflects my admiration for him, and, believe me, being a bright person can be a blessing or a curse. In the case of Miguel it was a blessing for everyone being around him and it was his decision to be like that.

Miguel was an exceptionally smart student, one of those that professors chat about in the bar at coffee time: have you met Miguel Blanco?

I don't know why I interested Miguel when I taught him statistical mechanics but I am most glad that I did. We mutually clicked. Before finishing his five-year long "licenciatura" (the spanish degree at his time) we started collaborating on different subjects and I met one of the best computational scientists that I have ever helped to train.

As a computational scientist, Miguel was absolutely intuitive: an exceptional programmer, as imaginative as a hard-working. His codes were extraordinary, well-documented and his articles
were even better. One of his codes, "GIBBS" is still the most cited work from our group. At the time of his death I was thinking of some ideas to improve the code, which we could not collaborate on, and his passing away was a shock for me, but not a surprise for him.

Miguel died young: being 41 years old. It was not in his plans and he even worked in his very last days trying to help the people left behind when the cancer was going to win its final battle. The last article coming out from his hands was in collaboration with Paul Popelier, finally published in JCP, and it is most fortunate that Paul is also here receiving a mostly deserved Bader award. Miguel would be as glad as I myself am.

Miguel was a man hopeful about life, about his work and about the people with whom he shared everything. Now we continue working with the ideas he helped to create: for instance working with the Wannier functions to calculate Bader's localization and delocalization indices, or all the ideas integrated in the IQA method, in which he deposited a lot of enthusiasm.

To the winner and all nominees of this MAB award: it is a most shining prize in which you have participated. As bright as Miguel was himself.

I won't be able to travel to Halifax for the Sagamore meeting, Believe me that I will be there as an unseen avatar when the MAB prize is finally given.

Life is most unfair when a good person is taken away from us, and Miguel was extremely good. I do not think I exaggerate if I say that everyone that met Miguel will miss him and that he remains and will remain very much alive in our minds.

Let me end with the deep words of an exceptional spanish poet:

“A las aladas almas de las rosas
del almendro de nata te requiero,
que tenemos que hablar de muchas cosas,
compañero del alma, compañero.”

Translating poetry is not easy at all and i won't even try, but the meaning of this beatiful final in “Elegía a la muerte de Ramón Sijé" is something like: "come to meet me at the pink flowers of the almond tree, that we have to talk on many things, my friend”.

Thanks for reading me,

Víctor Luaña
Richard F. W. Bader: A True Pioneer

It is an honor to be able pay tribute here to the remarkable career of Professor Richard F. W. Bader. Two of us (C.F.M. and T.A.K.) had the privilege to be among Richard’s many former graduate students and one of us (L.M.) has been a close friend to Richard and an admirer of his work since he first met him in 1974 during a crystallography symposium in Melbourne, Australia.

It is neither common nor easy to do something that is fundamentally new in science. This can be due both to inherent difficulties of the subject as well to biases that most of us have in favor of the familiar and against the unfamiliar. Richard Bader has been doing fundamentally new things for much of his career (Table 1). At times this has been met with considerable resistance. Fortunately, Richard has never wavered in his pursuit of new and useful ideas and, equally important, their publication. His hard work and persistence have led to explanations and quantification tools for many of the central concepts of chemistry and to the opening of an entire field of research—the topological analysis of electron density distributions—that has crossed the boundaries of theoretical chemistry to the laboratory bench of X-ray crystallography.

Founded on solid bases of quantum mechanics and observation, his seminal work, the Quantum Theory of Atoms in Molecules (QTAIM), is applied today by thousands of chemists, physicists, material scientists, molecular biologists, crystallographers, and others all over the world and has found applications from the physics of crystals to chemical biology and in the formulation of new strategies to design drugs. QTAIM has inspired the topological analysis of functions other than the electron density, a widely used example being the electron localization function (ELF).

Richard Bader is a true pioneer, being among the first to seriously ask and answer a number of fundamental questions about the physical basis for such powerful chemical concepts as atoms in molecules, functional groups, bonding, electron pairs and electron localization and delocalization, concepts that chemists and other scientists use every day. In 1963, a year before the historical discovery of the foundations of modern density functional theory (DFT), Bader and Jones wrote (J. Chem. Phys. 1963, 38, 2791—2802):

“The manner in which the electron density is disposed in a molecule has not received the attention its importance would seem to merit. Unlike the energy of a molecular system which requires a knowledge of the second-order density matrix for its evaluation (1) many of the observable properties of a molecule are determined in whole or in part by the simple three-dimensional electron-density distribution. In fact, these properties provide a direct measure of a wide spectrum of different moments averaged directly over the density distribution. Thus the diamagnetic susceptibility, the dipole moment, the diamagnetic contribution to the nuclear screening constant, the electric field, and the electric field gradient (as obtained from nuclear quadrupole coupling constants) provide a measure of (aside from any angular dependencies) \( r_{1}^{2} \), \( r_{1} \), \( r_{1}^{-1} \), and \( r_{1}^{-2} \), respectively. The electric field at a nucleus due to the electron density distribution is of particular interest due to the theorem derived by Hellmann (2) and Feynman. (3) They have demonstrated that the force acting on a nucleus in a molecule is determined by the electric field at that nucleus due to the other nuclei and to the electron-density distribution.”


This statement comes at a time when few were interested in the total electron density and its topography and topology as a vehicle for understanding and predicting chemistry. The first

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Milestones in Richard F. W. Bader’s Scientific Career\textsuperscript{a,b}

\begin{tabular}{|l|l|}
\hline
\textbf{Contribution} & \textbf{Year(s)} \\
\hline
Experimental and theoretical studies of solvent effects. Librational model of water solvent isotope effects. & 1954–1961 \\
Discovery of the first symmetry rules for predicting signs of vibrational interaction force constants and courses of chemical reactions. & 1962 \\
Detailed analyses of molecular charge density distributions. & 1963–1969 \\
Detailed analyses of Feynman forces on nuclei and studies of Berlin binding and antibinding regions. & 1968 \\
Detailed analyses of kinetic energy densities. & 1969, 1978 \\
First theoretical discovery of a Teller conical intersection. & 1971 \\
Discovery of relationship between regional transferability of charge densities and kinetic energy densities. & 1972 \\
Discovery of natural partitioning of molecules into mononuclear regions bounded by surfaces having zero flux of the gradient of the electron density. & 1971–1975 \\
The postulation of the existence of an atomic virial theorem. That is, the realization that fragments bounded by zero-flux surfaces have unique kinetic energy and for which a virial relationship \( \bar{E}(\Omega) = V(\Omega) + \bar{T}(\Omega) \) appear to apply. & 1971–1974 \\
Variational derivation of the significance of the zero-flux boundary condition and atomic virial theorem. & 1975, 1978 \\
Proof of the atomic virial theorem and Eilenfest theorem. & 1975, 1978 \\
Generalization of Schwinger’s principle of stationary action to open systems (atoms in molecules). & 1978, 1994 \\
Discovery of the bond path. & 1977, 1998 \\
Localization and delocalization of electrons in molecules through analysis of pair density distributions and Fermi hole distributions. & 1975, 1989, 1996, 1999 \\
Development of AIMDPC, a freely distributed computer program package for QTAIM analyses. & 1981 \\
Recovery of group additivity schemes via atomic and group contributions to molecular energies, volumes, dipole moments, vibrational absorption intensities, polarizabilities, magnetizabilities, etc. & 1993–2002 \\
Discovery of importance of atomic polarizability, in addition to atomic charges or charge transfer, in interpreting molecular dipole moments and dipole moment changes. & 1992 \\
Development of the IGAIM and CSGT methods. Analysis of magnetically induced current densities and atomic contributions to molecular magnetic response properties. & 1992–1996 \\
Discovery of structural homomorphism between the electron density and the virial field. & 1996 \\
Discovery of non-nuclear attractors. & 1987 \\
Discovery of the source function. & 1998 \\
Development of the localization and delocalization indices. & 1999 \\
Elucidation of the atomic origins of rotational and inversion barriers. & 1990 \\
First analysis of topology of crystalline charge density distributions. & 1994, 1995 \\
Discovery of the stabilizing nature of the closed-shell hydrogen–hydrogen (H–H) bonding interactions in molecules and crystals. & 2003 \\
\hline
\end{tabular}

\textsuperscript{a} A fully referenced version of this table can be found in the Supporting Information. \textsuperscript{b} The ordering of this list is not strictly chronological, but rather mainly logical and topical. The listed years or range of years are only indicative of the period where the groundwork related to the listed contribution has been published. In several instances, the work has been further developed at later dates and in some cases is still being actively developed at the time of writing.

Contour plots of electron densities in molecules, now commonplace, were published by the Bader group already in the early 1960s (Figure 1) along with deep discussions on their significance as carriers of key physical information about structure, bonding, and reactivity. Early studies of the electron density as well as kinetic energy densities by Bader and co-workers in the 1960s and early 1970s were enabled through a collaboration with Clemens C. J. Roothaan and his then former Ph.D. advisor and Nobel Laureate Robert S. Mulliken, both at the University of Chicago. Careful examination of the density maps ultimately led Richard and his co-workers to the realization that a regional similarity (transferability) of the electron densities between different molecules is associated with a corresponding transferability of kinetic energy densities.

Bader and Bedall discovered in 1972 that the real space of a molecule is naturally partitioned into mononuclear atomic regions, each bounded by surfaces having the property of zero flux in the gradient of the electron density. This partitioning appeared to result in a maximal and paralleling transferability of the electron and kinetic energy densities for each atom in a molecule. Because there can be multiple definitions of kinetic energy density, it is equally important that this unique partitioning yields the same atomic kinetic energy regardless of the kinetic energy density definition. On the basis of these observations, together with the implied transferability of atomic energies associated with experimental additivity schemes for heats of formation, Bader and Bedall postulated that the molecular virial relationship \( 2T + V = 0 \) (for stationary point molecular geometries) between electronic kinetic energy \( T \) and potential energy \( V \) may also apply to individual atoms in a molecule, \( 2\bar{T}(\Omega) + V(\Omega) = 0 \), and thus the energy \( \bar{E}(\Omega) \) of an atom \( \Omega \) in a molecule could be defined as \( \bar{E}(\Omega) = -\bar{T}(\Omega) \) in analogy with the molecular result \( E = -T \) that follows from the molecular virial theorem and \( E = T + V \).

Bader and co-workers later proved the postulated atomic virial relationship between the atomic kinetic energy and the atomic energy.
The virial of the Ehrenfest force density acting on an atom and its surface, the total atomic potential energy. The virial theorem for an atom in a molecule provided the basis for defining what had previously been thought unattainable, that is, a local, unique, straightforward and relatively easily calculable energy of an atom in a molecule. Atomic energies so defined are transferable in a manner paralling the atomic electron density distribution and, for stationary point geometries (and provided the molecular virial theorem is satisfied) are additive to give the total molecular energy when the sum runs over all the atoms or the energy of a group of atoms within the molecules if that sum runs over the atoms forming that group. This partitioning has allowed researchers a new perspective on understanding the energies of molecules, and the changes of these energies in different conformers or at different local minima or saddle points on the accessible potential energy surface. Such discussions of energy at an atomic resolution were previously thought to be impossible, but Richard sought the solution outside the traditional box by taking as the starting point the observable electron density.

The virial theorem has been generalized in a second way by Bader et al. into a local version. The local virial theorem relates a potential energy density, and the gradient form of the kinetic energy density, to the Laplacian of the electron density. The Laplacian of the electron density plays a central role in QTAIM and its topology faithfully recovers the atomic shell structure of isolated atoms as well as the Lewis and VSEPR models of bonded and nonbonded electron pairs of atoms in molecules and is useful for characterizing bonded interactions in molecules and for predicting reactive sites in molecules. Maps of the Laplacian of the electron density obtained from X-ray diffraction experiments followed by multipolar refinement fill the crystallographic literature, because these maps and their topography are now recognized to provide deep insight into the nature of chemical bonding. A noted example for such insight is the development of a complete real-space theory of the solid state by the group at Universidad de Oviedo (Spain) on the bases provided by QTAIM and its analysis of the electron density.

Figure 1. An example of Bader's early total electron density distribution maps (of the NH₃ molecule) published in the Journal of Chemical Physics' issue of 15 June 1963. Nowadays, 48 years later, plots of the density and of its associated gradient vector field and Laplacian fill journals of computational and theoretical chemistry and crystallography alike. (Reproduced with permission from the American Institute of Physics. Copyright 1963.)
Schrodinger's energy functional generalized to subspaces bounded by surfaces having zero-flux of the gradient of the electron density. The variational derivation of the atomic hypervirial theorem, followed shortly thereafter by the generalization of Schwinger's principle of stationary action to an atom in a molecule, marked the birth of QTAIM.

Simultaneously with solidification of the quantum mechanical underpinnings of QTAIM, the topological properties of the electron density were thoroughly explored by Richard and coworkers, and this work quickly blossomed into an entire coherent and consistent theory of molecular structure and structural stability used by theorists and experimentalists alike. The most important organizing principle in chemistry, that a molecule is a collection of atoms in real space with characteristic properties and linked together by bonds, and that a chemical reaction involves a rearrangement of atoms and making and breaking of bonds, was given full, quantifiable backing by QTAIM. Long before electron density functional theory became popular, or even generally known, among quantum chemists, Richard and his group had embarked on a program of thoroughly investigating electron density distributions in molecules. By the time density functional theory became mainstream, Richard and his group had developed an extensive and usable theory of the fundamental concepts of chemistry in terms of the electron density.

Another important development came from detailed analyses of electron pair density distributions by Bader and co-workers: the realization that the localization of an electron in a region within a molecule is determined by the corresponding localization of its associated Fermi hole. As a corollary, the delocalization of the Fermi hole reflects the delocalization of the electron in the molecule. This finding, combined with QTAIM, ultimately led to a precise determinations of the extent to which the electron population of an atom in a molecule is localized in the atom, the localization index, and the extent to which the electron population of an atom is shared with other atoms in a molecule, the delocalization indices. Interestingly and significantly, Bader and Heard discovered that the Laplacian of the electron density faithfully reproduces the spatial characteristics of electron localization and delocalization as revealed by the topology of the Laplacian of the conditional pair density.

It seems that whatever field Richard was involved in, however briefly, new ideas emerged. Another example is magnetic response properties. In their endeavor to understand molecular magnetic response properties of closed-shell molecules in terms of atomic contributions, Richard and a graduate student were led to calculate and analyze magnetically induced current density distributions. Using conventional single-gauge methods available to them at the time proved inadequate due to the practical problem of gauge-origin dependence, but the use of QTAIM saved the day because it encouraged the calculation of the current density distribution at a time, with the nucleus of each atom serving as the gauge origin for the current density distribution within the atom. This Individual Gauges for Atoms In Molecules (IGAIM) approach proved to be quite reliable in eliminating the gauge problem and predicting relatively accurate molecular magnetic response properties. The IGAIM method was soon generalized to the Continuous Set of Gauge Transformations (CSGT) method, a novel and practical method whereby a different gauge origin is used for each point in space and calculate molecular current density distributions and the molecular magnetic response properties they determine.

The IGAIM and CSGT methods enabled the thorough and correct topological analyses of magnetically induced current densities for the first time and the investigation of molecular magnetic response properties in terms of atomic and bonding contributions.

Besides pure and applied theoretical chemistry, perhaps no field has been impacted more by the work of Richard and coworkers than X-ray crystallography. The foundations of QTAIM emanate from the electron density that is the very object of experimental X-ray analysis. In the early days of electron density measurements by crystallographers, interpretation of results was hampered by an overdependence on "difference density" methods, which, however useful heuristically, suffered from ambiguous reference atomic densities and had little connection with quantum mechanical theorems. It is a fortunate circumstance that major advances in the ability to measure high resolution crystalline electron densities in the past few decades have coincided with the parallel development of the theoretical tools necessary to analyze and interpret them, viz., QTAIM. It is fitting that Richard and one of his graduate students at the time, P. F. Zou, were among the first to discuss and perform full QTAIM analyses of crystalline electron densities.

It is no exaggeration to point out that QTAIM analysis has revolutionized the understanding of accurate coherent X-ray electron density measurements, by bringing them into strong correspondence with the quantum mechanical theorems that underlie and make understandable molecular structure. The experimentally measured electron density zero-flux surfaces partition a crystal into atoms and functional groups with transferability properties that track experimental behavior and has led to the development of several transferable multipolar databases.

The electron density critical points allow quantitative analysis of bonding properties in crystals. It is of utmost significance to crystallographers to find that ridges of maximal electron density between nuclei, bond paths, unfailingly characterize attractive interactions, of every kind, weak and strong. To be emphasized is that all these topological properties of the electron density are available from analysis of the measurements obtained from X-ray diffraction experiments. Indeed, the fact that the analysis is exactly the same for densities whether experimental or theoretical is of importance. It is just such direct comparison of experimental and theoretical objects that makes understanding most complete and prediction possible.

In the earlier years of his career, Richard was an experimental physical organic chemist, before he switched to theory in the sixties. Even though Richard has spent most of his career as a theorist, his skill at the wet laboratory bench and outside the realm of quantum chemistry was equally exceptional. Together with his Ph.D. advisor C. G. Swain, he published a series of important papers on solvent isotope effects.

Perhaps one of the most significant early contributions of Richard was the use of molecular vibration theory, perturbation theory and molecular orbital theory to formulate the first symmetry rules to predict the signs of vibrational interaction force constants as well as possible pathways of chemical reactions. In this work, Richard cleverly showed that the lowest-lying excited state of a molecule or transition state that gives a nonzero transition density determines, by symmetry, the normal vibrational mode(s) that can lead to decomposition of a molecule or a transition state, thus allowing predictions of the course of some chemical reactions. A reading of these papers illustrates Richard’s detailed knowledge and appreciation of molecular orbital theory in classifying electronic states of molecules. The significance of
Richard’s work did not escape the notice of Kenichi Fukui, who stated in his 1981 Nobel Lecture:

“In this way, it turned out in the course of time that the electron delocalization between HOMO and LUMO generally became the principal factor determining the easiness of a chemical reaction and the stereoelective path, irrespective of intra- and intermolecular processes, as illustrated in Fig. 3. Besides our own school, a number of other chemists made contributions. I want to refer to several names which are worthy of special mention.

First of all, the general perturbation theory of the HOMO-LUMO interaction between two molecules was built up by Salem.22-25 One of Salem’s papers26 was in line with the important theory of Bader,27 which specified the mode of decomposition of a molecule or a transition complex by means of the symmetry of the normal vibration. Furthermore Pearson28 investigated the relation between the symmetry of reaction coordinates in general and that of HOMO and LUMO.”

(References in this passage as in Fukui’s Nobel Lecture, where his ref 26 is to the paper: Bader, R. F. W. Vibrational induced perturbations in molecular electron distributions. Can. J. Chem. 1962, 40, 1164–1175.)

It is particularly fitting to see a festchrift in this Journal where Richard has published 60 out of his 220 papers. Richard’s papers are often listed among the “Most Read” on the Journal’s web page. At the time of this writing, for example, his paper “Definition of Molecular Structure: By Choice or by Appeal to Observation?” is listed among the Journal’s “Most Read” in the past 12 months, while his paper in the present festchrift in his honor “Worlds Apart in Chemistry: A Personal Tribute to J. C. Slater” is the most read paper in the past month (June – August 2011). His papers are also often very highly cited (Table 2). For example, his paper “Bond Paths Are Not Chemical Bonds” is listed among the Journal’s Most Cited Papers in the last three years. And two of his classic papers are listed among the “All Time Top 20 Most Cited Articles published by the Journal”, his paper entitled “A Bond Path: A Universal Indicator of Bonded Interactions” (482 citations) and the one he coauthored with his co-workers, now Professors Xavier Pradera and Maggie A. Austen, entitled “The Lewis Model and Beyond” (348 citations). A third paper, also in the “All Time Top 20 Most Cited” is one on the “Characterization of a Dihydrogen Bond on the Basis of the Electron Density” by Professor Paul L. A. Popelier (428 citations) is also based on QTAIM. Another paper in this Journal that uses QTAIM to characterize hydrogen bonds, entitled “Characterization of C–H–O Hydrogen-Bonds on the Basis of the Charge-Density” (by Popelier et al.), has received 776 citations, according to the ISI at the time of writing.)

In closing, it is an impossible task to do justice to a scientist of the standing of Richard F. W. Bader in a short tribute such as this. We wish him and his family, affectionately, a happy 80th birthday and thank him for his friendship and invaluable and lasting contributions to chemistry and physics.

Chérif F. Matta
Mount Saint Vincent University

Lou Massa
City University of New York

Todd A. Keith
Semichem, Inc.

ASSOCIATED CONTENT

Supporting Information. A version of this tribute article with embedded literature citations and a list of 172 bibliographic references. This information is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

C.M.: e-mail, cherif.matta@msvu.ca; telephone, +1-(902)-457-6142; fax, +1-(902)-457-6134. L.M.: e-mail, lmassa@hunter.cuny.edu; telephone, +1-(212)-772 5330; fax, +1-(212)-772-5332.T.A.K.: e-mail, todd@semichem.com; telephone, +1-(913)-268-3271; fax, +1-(913)-268-3445.

Robert Farrell Stewart (1936–2015)*

Mark A. Spackman* a

School of Chemistry and Biochemistry, University of Western Australia, Perth, WA 6009, Australia

*Correspondence e-mail: mark.spackman@uwa.edu.au

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Robert (Bob) Farrell Stewart passed away on 16 September 2015. Born and raised in Seattle, Bob obtained his BA in Chemistry from Carleton College in Minnesota in 1958. It was there he met classmate Janet Trussell, who became his wife in 1959, and together they went to Pasadena where Bob obtained his PhD in Chemistry from Caltech in 1963. Bob's mentor there was Norman Davidson, and his thesis title Polarized absorption spectra of purines and pyrimidines reveals that although more widely known as a theoretician, Bob began his research career as an experimentalist.

From Pasadena Bob went to Seattle as a Postdoctoral Fellow of the US Public Health Service at the University of Washington. There he met Lyle Jensen and soon became interested in theoretical aspects of X-ray crystallography. Because of the very accurate X-ray data being collected in Jensen's laboratory, and the advent of full-matrix least squares, it was becoming apparent that the hydrogen-atom scattering factor then in use was inadequate, resulting in isotropic thermal parameters for hydrogen that were systematically low, and even negative. Bob saw that it would be more appropriate to use the scattering factor for a bonded hydrogen atom, derived from the wavefunction for molecular hydrogen. The report of this work, Coherent X-Ray Scattering for the Hydrogen Atom in the Hydrogen Molecule, has become one of the most widely cited papers in the crystallographic literature, and this bonded hydrogen-atom scattering factor is now universally adopted, having appeared in International Tables for Crystallography for several decades.

Bob and Jan Stewart, with their children Robert and Annamarie, made Pittsburgh their home in 1964. Bob was first at the Mellon Institute and then Carnegie Mellon University after its merger with Carnegie Institute of Technology in 1967. There he pursued his interest in the study of nuclear and electronic charge distributions in crystals – later known as ‘charge-density studies’. His first paper on Generalized X-Ray Scattering Factors appeared in 1969, and built on the earlier work of Barrie Dawson and Kaarle Kurki-Suonio. This was followed by a series of papers in The Journal of Chemical Physics that developed the use of generalized scattering factors to extract electron-density information as well as physical properties of molecules. Three papers –
one of which remains unpublished – resulted from Bob's award of an Alfred P. Sloan Fellowship (1970–1972), which enabled him to further develop his ideas while visiting the late Ted Maslen in Perth, Western Australia, in 1971. In 1976, some time after his return from Perth, Bob published Electron Population Analysis with Rigid Pseudo-atoms, which laid out the multipole model now widely applied in deriving the charge density in crystals from experimental X-ray and neutron diffraction data.

Less well known is Bob's role at the same time in the development of Gaussian basis sets, a collaboration with John Pople, who had moved to Carnegie Institute of Technology in 1964. The starting point was Bob's 1969 paper Small Gaussian Expansions of Atomic Orbitals, which acknowledged Pople for his encouragement, and which included this understatement: `The major utility of these orbitals is for the evaluation of generalized scattering factors for x-ray diffraction studies...It should also be mentioned, however, that the Gaussian expansions reported here may be useful for ab initio calculations in quantum chemistry.' Pioneering applications of these STO-nG basis sets to molecular-orbital calculations were co-authored with Warren Hehre and John Pople between 1969 and 1970.

The decade of the 1970s was exceptionally productive for Bob. After his return from Perth he had lost interest in the single-exponential work and devoted an increasing effort to the solution of the equations for deriving radial functions of multipole expansions for diatomic molecules. With graduate students John Bentley and Joel Epstein, Bob published a substantial body of this work, investigating X-ray scattering (total and coherent), electron scattering, core deformation, vibrational averaging and vibrational force constants. The key publication from 1975, Generalized X-ray Scattering Factors in Diatomic Molecules, demonstrated not only that generalized scattering factors determined from finite multipole expansions about the nuclei necessarily satisfied certain expectation values of the diatomic molecular charge density, but outlined a mathematical procedure for their determination via least squares. The paper presented monopole, dipole and quadrupole scattering factors for the hydrogen pseudoatom in H2, and concluded that these `could be instrumental in a more accurate determination of the time-average proton positions in organic molecular crystals'. This preceded by several decades the use of transferable pseudo-atoms from various databases, or iterative refinement of `Hirshfeld atoms'.

Bob recognized very early that the pseudoatom parameters that describe a molecular electron-density distribution could also be used to derive other important chemical and physical properties. When I joined his group in 1980 Bob had already developed VALRAY, a very extensive system of computer programs for least-squares refinement against X-ray diffraction data to obtain pseudoatom parameters, and the code for mapping properties of molecules and crystals was in its infancy. Over the following three years we expanded and calibrated the code for computing the electrostatic potential, electric field, electron density and electric field gradient via several Fourier and direct-space strategies. This was later extended to include properties from Richard Bader's theory of Atoms in Molecules (AIM), notably through Bob's collaboration with Claus Flensburg in Copenhagen. For many years Bob used VALRAY as his primary research tool for careful calibration of experimental results against those obtained from ab initio theory.

A significant factor in Bob's considerable impact on modern charge-density analysis came through his presence at, and contributions to, several key international meetings. Many of us first got to know Bob in 1977 at the two-week-long Bat Sheva Seminar on Electron Density
Mapping in Molecules and Crystals, organized by Leslie Leiserowitz, Joel Bernstein, Phillip Coppens, Fred Hirshfeld and others, held at the Weizmann Institute in Israel. The lecture notes from the meeting, published as a special issue of the Israel Journal of Chemistry, became a reference text for the field for many years. The following year Bob participated in a NATO Advanced Study Institute, organized by Pierre Becker in Arles, on Electron and Magnetization Densities in Molecules and Crystals; a comprehensive book of proceedings was published in 1980. Another NATO Advanced Study Institute, on The Application of Charge Density Research to Chemistry and Drug Design, was organized by George Jeffrey and Juan Piniella in Spain in 1990. The 1991 book of proceedings included an important chapter by Bob, Electrostatic Properties of Molecules from Diffraction Data, that included examples of the electrostatic potential, Laplacian and (3,−1) critical points of the electron density, based on rigid pseudoatom fits to experimental diffraction data measured by Bryan Craven's group at the University of Pittsburgh. Bob was also a regular speaker and active participant in the triennial Gordon Research Conferences on Electron Distribution and Chemical Bonding held at Plymouth State College between 1978 and 1995.

Bob's influence also grew through visits to research groups overseas. In addition to his time in Perth, Bob spent productive periods at the Universities of Groningen, hosted by Aafje Vos, and Copenhagen, hosted by Sine Larsen. His time in Groningen resulted in the important 1979 paper on Mapping of Electrostatic Properties from Bragg Diffraction Data, as well as A Theoretical Study of Elastic X-ray Scattering, jointly with Dirk Feil in 1980. Bob's first visit to Copenhagen was for half a year in 1991, and it coincided with his new focus on implementing aspects of Bader's AIM theory for experimental electron densities. This sabbatical in Copenhagen initiated a very fruitful and productive collaboration that continued with annual visits each summer for more than a decade. Bob took an active part in, and had a great impact on, the scientific life of Sine Larsen's group, including co-supervision of graduate students Claus Flensburg, Henning Osholm Sørensen and Anders Østergaard Madsen.

Bob stood out as a scientist of the old school, who only wanted to publish things that he felt were done in the `right' way. But he often struggled with recognizing when good was good enough, and from the early 1980s he simply stopped publishing at the rate required to secure funding, often taking his name off papers because he wasn't wholly satisfied. In 1979 Bob wrote to me – a young graduate seeking to join him as a postdoctoral fellow – “I do not operate big time `show-biz' research programs – with such endeavors most people sacrifice quality for quantity...A critical evaluation, as well as intellectual honesty, are the essential ingredients to scientific research. And I will hold the line on that as long as I can manage."

Bob was a very modest person, and his scientific rigour was essential to the development of electron-density research. He was a great scientist in a class of his own, and he has left an outstanding legacy of original work, much of it still underappreciated. He will be fondly remembered and missed by many, as the host of Friday afternoon `seminars' at the Craig Street Inn, for his remarkable knowledge and love of Fourier transforms, American football and the theory and application of X-ray scattering, as a valued friend and mentor to many young scientists, and as an enthusiastic and stimulating colleague.
Philip Coppens (1930–2017)*

Pierre Becker a*

a UMR SPMS, CentraleSupelec, Grande Voie des Vignes, 92295 Chatenay Malabry Cedex, France
*Correspondence e-mail: pierre.becker@centralesupelec.fr

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Professor Philip Coppens, born in 1930 in the Netherlands, died suddenly on 21 June 2017 while he was leaving his office at Buffalo University. This was a tremendous shock (both in scientific and personal terms) for the international scientific community, particularly materials science and crystallography. Since his first publications, which were focused on the potential impact of crystallography on the study of the quantum behavior of matter, he attracted young scientists from the whole world. He always emphasized the complementary capacities of his co-workers and helped them to develop their own successful careers. He was undoubtedly the ‘father’ of global developments in the study of the electronic behavior of matter (from simple systems to biological systems) using X-ray/neutron (X–N) scattering. Many young researchers who had recently enjoyed fascinating cooperations with Professor Coppens in the field of time-resolved crystallography, a prime area for future studies, were deeply dismayed to hear the sad news.

Philip Coppens started his research with Caroline MacGillavry in the area of crystal structures and photochemistry. His PhD (Amsterdam, 1960) was mainly carried out at the Weizmann Institute in Israel. He approached the study of the electronic behavior of condensed matter (at or out of equilibrium) through intense cooperation with Fred Hirshfeld and Gerhard Schmidt. One main result concerned the differentiation of the photo-induced behavior of two polymorphs of p-nitrophenol (at a time where lasers did not yet exist).

Just after his PhD, he was recruited by Walter Hamilton at Brookhaven National Laboratory (including stays at the Weizmann Institute and various places in Europe). His innovative work on X–N diffraction complementarity aided the study of the electronic behavior of solids. His paper in Science in 1967 [Coppens, P. (1967). *Science*, **158**, 1577–1579] showed the electron deformation density of s-triazine and created a worldwide research axis. He focused on the

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importance of mastering `real' aspects of X-ray and neutron diffraction (such as absorption, extinction and thermal effects) for obtaining trustworthy electron density. The quality of his research led to his appointment as a professor at Buffalo University, where he stayed thereafter with his family. Philip and Robert Stewart were the source of every group that developed research on charge, spin and momentum density across whole continents. In cooperation with Richard Weiss and Vedene Smith, he also brought about important triennial conferences such as the Gordon Reseach and Sagamore conferences.

His paper in Science attracted me, as it gave a concrete sense to molecular wavefunctions, and I joined his group with my family for my PhD at the end of 1972. Amazingly, I was asked to work on extinction (both for X-rays and neutrons) and to propose a workable model; he also asked me to optimize step-scanned signal versus noise data. This was very hard, but all members of the lab used to exchange ideas, in particular through weekly meetings. It was said that Philip first experienced time-resolved research, since he came to us every 15 minutes asking how we had been improving! The experience was unforgettable and the final gift was the determination of the deformation density in tetracyanoethylene (with F. K. Ross), revealing simple, double and triple bonds plus lone pairs: at that time, quantum computations were not possible for such a molecule.

Philip had a fantastic chemical intuition and always put emphasis on finding the potential complementary talents of his co-workers. His priority was to further our international scientific recognition – he never said 'I did', but always emphasized our work. This was extremely positive and opened up long-term international collaborations for us. Each of us could create personal groups and suggest young scientists who could interact with Philip. Another fundamental quality of Philip struck me concerning extinction: when the theoretical strategy was validated by referees, he proposed a simple scheme that would be easily transferable in refinement processes.

A fundamental scheme was proposed by Niels Hansen and Philip: the multipolar development of charge density, which has been used by all groups for nearly 40 years. With Guru Row, we proposed a complementary approach concerning the extension of radial functions, the application of which fits the Slater model for atomic orbitals. It also led to a first joint charge–spin density study with Tibor Koritzansky. The joint refinement of charge, spin and momentum densities is now a key issue in advanced crystallography (for the groups of Beatrice Gillon, Jean Michel Gillet and Claude Lecomte, and at Spring8, among others) and is leading to a promising project towards 'quantum crystallography'.

Another important approach was developed by Claude Lecomte's group, in parallel with Philip's group, and concerned the electronic behavior of proteins. A substantial database built on charge partitioning of molecular groups present in proteins was developed. Crystallography thus allowed this fundamental domain to be approached.

Philip also worked on structural evolution in phase transitions (e.g. the metal–insulator transition for TTF–TCNQ with Vaclav Petricek, involving incommensurate modeling) and charge-density evolution under an applied electric field. He also interacted strongly with Anatoly Volkov (from Siberia) and Tibor Koritzansky.
In 1997, Philip thought it was time to move to his `childhood dream': photocystallography. As usual, his intuition about which chemical compounds to study was correct. The first we tried was sodium nitroprusside (showing long-lived excited states), which was studied in the lab using laser flashes at low temperature. Then he used synchrotron sources, including at Brookhaven National Laboratory, with picosecond pulses, then the Argonne Advanced Photon Source. He welcomed many motivated young scientists from both Krystok Woszniak's and Claude Lecomte's groups, who became involved in fascinating new studies, such as those leading to the observation of the 0.28 Å contraction of Pt—Pt bonds in Pt$_2$(P$_2$O$_5$H$_2$)$_{44}^-$. at 16 K for which the duration of the excited state was 50 µs. Then with Jason Benedict he developed studies of the time-dependent behavior of nanoparticles, again starting a new boundless area of solid-state science.

On 22 October 2016 Jason Benedict organized a retirement ceremony for Philip. It was an unforgettable day, where many collaborators came and enjoyed the strong long-term friendships that had started from their work with Philip.

Owing to his unique influence on developments in crystallography, Philip received many prizes, including the Aminoff Prize in 1996 and the Ewald Prize in 2005. He was President of the International Union of Crystallography (IUCr) from 1993 to 1996, a member of the IUCr Executive Committee from 1987 to 1999, and a member of the IUCr Commission on Charge, Spin and Momentum Densities from 1972 to 1981, the Commission on Neutron Diffraction from 1975 to 1978 and the Commission on Journals from 2002 to 2015. His book X-ray Charge Densities and Chemical Bonding (IUCr/Oxford University Press, 1997) summarized in a highly pedagogical way the key aspects of his contribution to crystallography.

Philip remains an eternal guide for us, and his spirit will continue to guide international scientists.
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