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Alexander I. Boldyrev and the Frontiers of Chemical Bonding

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Abstract

The academic career and scientific achievements of Professor Alexander I. Boldyrev of Utah State University are briefly reviewed.

In late 2021, friends and colleagues of Professor A. I. Boldyrev of Utah State University will congratulate him on his seventieth birthday. A native of Novokuznetsk in southwestern Siberia, he matriculated at Novosibirsk University and began his research career at the Institute of New Chemical Problems of the Academy of Sciences of the Union of Soviet Socialist Republics. In 1978, he defended his Candidate of Sciences dissertation under the auspices of Moscow State University. His Doctor of Sciences degree was conferred by the Moscow Physico-Chemical Institute in 1986, where he taught and performed research. He was an Advanced Senior Researcher in the Institute of Chemical Physics of the USSR Academy of Sciences from 1988 to 1991. During 1990 and 1991, he was an Alexander von Humboldt Fellow in the Institute of Organic Chemistry of Erlangen-Nurnberg University in the Federal Republic of Germany and collaborated with Professor Paul Schleyer. Shortly thereafter, he came to the United States and began a long and fruitful collaboration with the group of Professor Jack Simons at the University of Utah that resulted in dozens of widely cited publications.

Since 1999, Professor Boldyrev has been a member of the faculty in the Department of Chemistry and Biochemistry at Utah State University, where has been Professor since 2005 and received many honors, such as the 2008 Utah Award of the American Chemical Society and the 2009 D. Wynne Thorne Award, USU's highest distinction for research. Recently he was named the first R. Gaurth Hansen Professor. In 2017, he was recognized as USU's Graduate Mentor of the Year, an honor that celebrates the care, guidance and scientific insight that have propelled the aspirations and careers of his former and present students, who have been impressed by his steadfast, unassuming dedication to science and young scientists.

Long before Schrödinger's equation, the Pauli exclusion principle or the Born-Oppenheimer approximation, chemists began to think of the properties and transformations of matter in terms of three-dimensional arrays of atoms. Geometrical concepts suffused the discourse that mapped point-wise changes in these arrays to the synthesis of new substances and that related reaction energies with

the formation and rupture of bonds between neighboring atoms. Chemists became confident that structural knowledge is a reliable precursor to control over matter. Pictures of molecules that display bonding relationships between atoms were inculcated in the minds of students almost as early as the laws of stoichiometry. G. N. Lewis's pairs of dots were represented by lines when chemists pushed electrons with curly arrows in their synthetic and mechanistic schemes.

Professor Alexander Ivanovich Boldyrev would generalize this tradition from its familiar jurisdiction of organic chemistry to the rest of the periodic table, for he believes that qualitative, structural concepts of chemical bonding provide the best way to stimulate discovery. One of his recurring themes is the revival of electron-pair concepts that accommodate multi-center delocalization, but only when it is necessary to surpass the two-center paradigm. Preference for localized pictures in his work leads to the identification of multi-center pairs that often confer enhanced stability on a molecule. His aim is to enable chemists to draw molecules and the electron pairs that determine their chemical properties.

The insights that follow from this approach to molecular structure are necessarily qualitative, but Boldyrev's calculations typically employ methods of quantitative accuracy on species that have been or are likely to be synthesized and precisely interrogated by experiment. His qualitative conclusions on structure and bonding therefore open doors that others may confidently traverse. Speculation alternates with verification in his computational studies and in his collaborations with experimentalists.

Dialectics between electronic-structure theorists and practitioners of anion-photoelectron spectroscopy such as Lai-Sheng Wang, Kit Bowen and Carl Lineberger have proven especially fruitful. Specialists in the latter field have developed a versatile array of synthetic and separation techniques that precede spectroscopic interrogation. Their experiments associate electron binding energies to species whose masses are precisely known. Usually there is no doubt of the chemical formula of an anion under study, but the relevant structures remain to be imagined.

At this point, computational investigation begins with thorough searches of plausible structures and energetic disqualification of isomers that are unlikely to be present in the experimental sample. Versatile, unbiased techniques for procuring structures with genetic and coalescence-kick algorithms developed by Alexandrova, Averkiev and Boldyrev have increased the efficiency of these necessary, initial steps and enabled the systematic study of unprecedented structures with tens of atoms.<sup>1-3</sup> The next phase, prediction of the electron detachment energies of the most stable candidates, is crucial, for a detailed assignment often suffices to end further speculation on the structures that are responsible for the spectra. High computational accuracy is required, for semiquantitative agreement between theory and experiment regarding a single spectroscopic peak may not be enough to establish the presence of a structure or to exclude another. Agreement on several electron detachment energies frequently provides a convincing understanding of how spectra arise from the highest occupied orbitals of an anion. Calculations on energy differences of anionic and uncharged ground states of a given symmetry type may employ the usual methods of *ab initio* quantum chemistry when feasible or, after proper calibration, density functionals. Direct methods for evaluating electron binding energies that can yield many states of a given symmetry classification have been employed effectively by Boldyrev and coworkers since his first collaborations with V. G. Zakrzewski in 1989.<sup>4</sup> For example, in the assignment of Wang's photoelectron spectrum of  $\text{LiAl}_4^-$ , *ab initio*, electron-propagator calculations produced agreement within 0.1 eV of peaks corresponding to four, final, electronic states of the uncharged,

metallic cluster.<sup>5</sup> These results and calculations on related species provided convincing evidence for the existence of a planar  $\text{Al}_4^{-2}$  species of unusual stability.

Regardless of the rigor and precision of their methods, Boldyrev and his collaborators do not remain content only with numerical agreement between computation and experiment. Searching for the significance of their results in the context of chemical concepts of bonding is their final stage of inquiry. In the case of  $\text{Al}_4^{-2}$ , the choice of electron-propagator methodology furnished a bridge between *ab initio* prediction and qualitative interpretation, for each electron-binding energy was associated to a probability factor (pole strength) of the corresponding Dyson orbital. (The latter, one-electron function is an overlap between an initial, anionic state and a final, uncharged state and its probability factor is a measure of the validity of a one-orbital picture of the transition between the states.<sup>6</sup>) Delocalized  $\pi$  and  $\sigma$  Dyson orbitals with probability factors near unity revealed multi-centric patterns of bonding that would reappear in subsequent discoveries on main-group clusters.

Delocalized Dyson orbitals from correlated, *ab initio* theory can provide excellent accounts of spectra, but localized orbitals may be ascribed to a molecular structure even in the absence of calculation. The influence of the latter notions therefore endures in the thinking of chemists, but it does not command exclusive loyalty. Zubarev and Boldyrev's descriptive compromise, known as Adaptive Natural Density Partitioning (AdNDP),<sup>7</sup> aims to extract simple, one-center and two-center pairs of electrons from reduced density matrices to the greatest extent possible while embracing multi-center pairs when necessary. This middle path de-emphasizes potentially numerous resonance forms and generates pictorial representations of electron pairs. It builds on the Natural Bond Orbital<sup>8,9</sup> analysis of Weinhold and coworkers by identifying electron pairs of ascending multi-center character without limitation to two-center or even three-center bonds. In its most successful applications, occupation numbers near two are easily identified. This approach also reveals cases where localized, electron-pairing notions have less qualitative validity.

The emergence of multi-center electron pairs from qualitative analysis of electronic structure has led to a broader recognition of the orbital origins of enhanced stability that is not confined to  $\pi$ -delocalized, organic molecules. Boldyrev has shown that multi-center,  $\sigma$  bonding can have a powerful role in stabilizing main-group clusters, including cases with tetra-coordinated, planar carbon atoms and peripheral, delocalized pairs of electrons.<sup>10,11</sup> Aromaticity and anti-aromaticity concepts expressed in terms of electron-counting rules for  $\pi$  and  $\sigma$  electrons have been formulated to facilitate recognition of relationships between structure and stability.<sup>5,12</sup> The collaboration between the Boldyrev and Wang groups has produced an array of bonding patterns in boron and boron-metal clusters that display high coordination numbers in planar geometries,<sup>13-16</sup> structural analogues of polycyclic aromatic hydrocarbons,<sup>3,17,18</sup> molecular wheels and Wankel engines.<sup>13,19</sup> In each case, quantitative agreement between calculations and experiments obtains and the results are interpreted in terms of qualitative bonding concepts.<sup>19,20</sup>

This approach to understanding structure and bonding has been extended to periodic systems.<sup>21</sup> Perspicuous analysis of six-center electron pairs in graphene,  $\text{BC}_3$  honeycomb sheets and functionalized graphene has built bridges between traditional chemical concepts and those of condensed-matter physics.<sup>22-24</sup> Periodic double-helix structures that recapitulate bonding patterns seen in small clusters of lithium and phosphorus have been discovered.<sup>25</sup>

The antecedent to this trajectory of discovery was an interest in the electronic structure of molecular anions and associated concepts of electronegativity. In the early 1980s, Gennady Gutsev and Boldyrev began density-functional studies of electronegative species that culminated in a highly influential review on molecules of high electron affinity.<sup>26</sup> The champions of this search were dubbed super-halogens, i.e. molecules with greater electron-accepting powers than atoms of the halogen family. Experimental confirmation via anion photoelectron spectroscopy in collaboration with Wang eventually followed.<sup>27</sup> Zakrzewski and Boldyrev demonstrated the capabilities of electron-propagator methods in the prediction of the electron detachment energies of anions and in the assignment of ground and excited final states of super-halogens.<sup>28</sup> The search for super-halogens and demonstrations of their ability to extract electrons from other species remain favorite subjects for computational chemists. Related quests for ever-stronger super-acids (i.e. Brønsted-Lowry proton donors) and super-oxidizers continues to stimulate interest in super-halogens.<sup>29</sup>

The identification of super-alkalis (molecules with lower ionization energies than those of the alkali atoms) is another lasting response to the early explorations in the 1980s of Gutsev and Boldyrev with discrete-variable-method  $X\alpha$  calculations.<sup>30</sup> Experimentally determined record minima<sup>31</sup> have followed predictions made with a variety of computational techniques.<sup>32-34</sup>

Multiply charged anions (MCAs) that are stable in the gas phase also were tackled by Boldyrev and collaborators.<sup>35, 36</sup> The necessity of counter-ions or solvents in the chemistry of otherwise metastable entities as familiar as the sulfate and phosphate ions was demonstrated computationally.<sup>37</sup> The ability of metal-halide MCAs to delocalize charge over many halide centers was shown to be a recurring feature of these species.

Boldyrev and Simons have made important contributions to understanding of Rydberg molecules wherein an electron occupies a diffuse orbital that is composed chiefly of non-valence atomic constituents. They identified Rydberg molecules that also are super-alkalis and explored the ability of these unusual species to form chemical bonds<sup>38-40</sup> and to participate in Rydberg-covalent bonds.<sup>41</sup> This work anticipated recent inquiries into the formation of diffuse chemical bonds between solvated electron precursors.<sup>42, 43</sup>

In another set of collaborations with an experimental group, isoelectronic analogies between atoms and anions have been exploited by Boldyrev and Bowen in the discovery of anions that display unprecedented concatenations or multiple bonds between main-group elements.<sup>44-46</sup>

A persistent desire to systematize basic chemistry also led Boldyrev to investigate electron configurations and electronic angular momenta of diatomic molecules with a view toward creating a periodic table of these small, fundamental species. In the process of performing *ab initio* calculations of predictive quality, several misconceptions were discovered and opportunities for additional discovery were revealed.<sup>47</sup> The periodic tables that emerged from this work illustrate the utility of simple Aufbau principles in the recognition of patterns in chemical properties.

Boldyrev's computational works consistently display a respect for symmetry as a means of understanding and classifying in chemical bonding theory. This interest has spanned nuclear as well as electronic degrees of freedom in his work on non-rigid, molecular Hamiltonians and their symmetry properties.<sup>48, 49</sup>

The International Conference on Chemical Bonding, an important venue for discussion and exchange of ideas, has been organized several times by Boldyrev, Alexandrova, Wang and Natalia Boldyreva. This meeting, which takes place on the Hawaiian island of Kauai, has gathered scientists from many countries and disciplines since its first occurrence in 2013.

In small molecules, unusually stable anions, boronic and metallic clusters or systems with diffuse charge density, Boldyrev's relationships between structures and electron pairs tend to be formulated as follows. First, recognize lone pairs and two-center-bond pairs whenever possible; avoid describing these electrons in terms of delocalized orbitals. Second, describe the delocalization of the remaining valence electrons in terms of multi-center orbitals instead of recruiting multiple resonance forms that are based on localized, two-center bonds. Boldyrev would identify as many bicentric, Lewis pairs as rigorous calculations allow but also as many delocalized pairs as these calculations require. Third, the latter pairs should be confined to the smallest number of atoms that is compatible with an electron count of approximately two.

This approach embraces the simplicity and familiarity of Lewis's concepts, but avoids oversimplification. Applying the principle of conceptual economy, it introduces delocalization only as needed.

Two of us (JS and JVO) have known Professor Boldyrev for 30 years, admired his publications even before we met him and continue to anticipate his latest work. The remaining author (AA) is a former doctoral student who appreciates the formative influence he has exercised on emerging scholars. Professor Boldyrev's friends and colleagues continue to draw inspiration from his dedication and creativity and express their gratitude to him for his friendship, helpful insights and wise counsel.

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