JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

Counting Electrons in Electrides

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Cite This: https://doi.org/10.1021/jacs.3c10876
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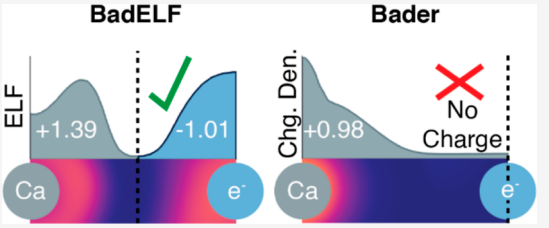
ABSTRACT: The selection and design of charge integration methods remain an outstanding challenge in materials chemistry. In complex materials like electrides, this challenge is amplified by the small charge and complex shape of electride wave functions. For these reasons, popular integration methods, such as the Bader method, usually fail to assign any charge to the bare electrons in an electride. To address this challenge, we developed an algorithm that instead partitions the charge based on the electron localization function (ELF), a popular scheme for visualizing chemically important features in molecules and solids. The algorithm uses Bader segmentation of the ELF to find the electride electrons and Voronoi segmentation of the ELF to identify atoms. We apply this method, "BadELF", to the quantification of atomic radii and oxidation states in both ionic compounds and electrides. For ionic compounds, we find that the BadELF method yields radii that agree closely with Shannon crystal radii, while the oxidation states agree closely with the Bader method. When they are applied to electrides, however, only the BadELF algorithm yields chemically meaningful charges. We argue that the BadELF method provides a useful strategy to identify electrides and obtain new insight into their most essential property: the quantity of electrons within them.



INTRODUCTION

Society needs new materials with extreme properties to address outstanding challenges in energy, computation, and medicine. Among such materials, electrides offer some of the most extreme properties, including electrical conductivity that rivals that of silver,[1,2] efficient reduction of N_2 and CO_2,[3,4] ultrafast ion transport for batteries,[5,6] and ultralow work-function electron emitters.[7,8] The most important characteristic of electrides—their defining quality—is that electrides are so electron-rich that electrons are ejected from atomic orbitals and are instead localized in the interstitial spaces between atoms. The presence of bare electrons in a solid material is a surprising observation but is supported by an increasing variety of experimental and computational approaches.[1,9−11] Despite these advances, however, it remains fundamentally challenging to quantify the number of bare electrons within an electride.[1,9−11]

The challenge of quantifying electride electrons arises for several reasons. First, there is no universally correct approach for quantifying charge, and there are many different methods depending on the purpose.[12−16] Second, electride sites contain only one or two electrons, in contrast to the large number typically found on nearby atoms. Because of this disparity, the electride charge density can be buried under the much larger atomic charge density. When this occurs, it can be difficult or impossible to separate the total charge density into its separate contributions.[17] In fact, methods that analyze the shape of the total charge density, such as the Bader method,[12] often fail to separate the electride and atomic regions. Third, the electride electron density is often unusually shaped—e.g., cylindrical (1D) or planar (2D).[1,9−11] Therefore, charge quantification methods that project the total charge onto spherical basis orbitals[15] might not be suited for the analysis of electrides that have nonspherical charge densities. Fourth, the electride charge is not bound to any atomic nucleus, so methods that measure charge by perturbing atomic nucleii[14] are not possible for electrides.

A hint of how to solve this problem appeared several decades ago, however, with the advent of the electron localization function (ELF).[18] The ELF, which takes values between zero and one, is calculated on a regular 3D grid across a unit cell. At each position, the ELF calculates the contribution to the kinetic energy density from each wave function. If only one wave function contributes, as in a covalent bond or lone pair—or, crucially, the bare electrons of an electride—the ELF approaches a value of one and the electrons are said to be localized. In contrast, when many wave functions contribute to the kinetic energy density, the ELF approaches zero, and the electrons are delocalized. Because high ELF values identify chemically meaningful features like lone pairs and bonds, the ELF has been used to

Received: October 2, 2023
Revised: November 1, 2023
Accepted: November 3, 2023

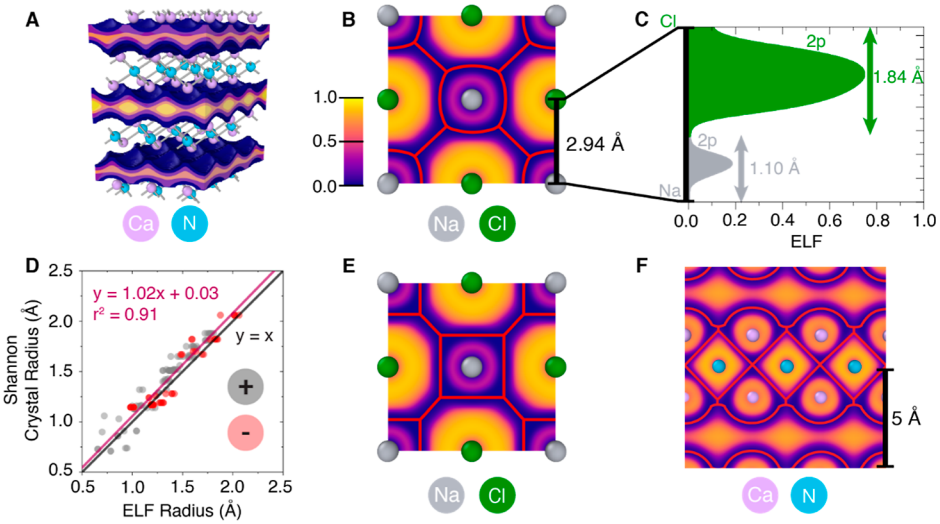


Figure 1. (A) ELF of the electride electrons in Ca_2N. (B) section of NaCl ELF with overlaid zero-flux partitioning surfaces demonstrating the nearly spherical Na^+. (C) ELF along a line from Na to Cl with labeled ELF radii. (D) Comparison of ionic radii found using ELF versus the respective Shannon crystal radii. The ELF radius is the distance from an atom to the closest local minimum in the ELF along an interatomic bond. Ions (N = 129) were selected from structures based on the availability of Shannon crystal radii. The BadELF partitioning was applied to NaCl (E) and Ca_2N (F), with dividing surfaces overlaid on a 2D slice of the ELF. Atoms that lie in the plane of the slice are overlaid on each ELF plot.

subdivide atoms, molecules, or solids to assign charge.[19] In fact, where comparison to known values was possible, absolute errors below 0.2 electrons and relative errors below 5% were demonstrated.[20] Although ELF plots are typically used to visualize electride electrons and although ELF-based partitioning can be highly accurate, it has not been applied to electrides. Therefore, it remains unclear whether such a method could address the long-standing challenge of quantifying bare electrons in electrides.

In this article, we develop this method into an algorithm that quantifies charge in crystalline solids. The algorithm, which we introduce as "BadELF", uses the Bader concept of dividing a 3D volume using local minima. Unlike the standard Bader method, we search for local minima in the ELF. Partitioning of electride electrons follows a zero-flux surface partitioning scheme like traditional Bader analysis, while partitioning of atoms is done using Voronoi-like divisions. These divisions define nonoverlapping volumes within which the charges are integrated. To benchmark this algorithm, we compared the oxidation states obtained by the BadELF and Bader methods using a selection of ionic compounds. We found that the BadELF and Bader methods yield similar results for these benchmarks. We then applied the method to a wide selection of electrides. We find that the BadELF method yields intuitive and chemically meaningful results for a variety of electrides, therefore providing a general strategy to characterize and understand the electrons within these fascinating materials.

RESULTS AND DISCUSSION

In the initial version of our algorithm, we sought to quantify atomic and electride charges by modifying the Bader algorithm as implemented by Henkelman.[21] The Bader algorithm is typically used to separate atoms at zero-flux surfaces of the charge density. A zero-flux surface is a 2D surface, where the charge density is at a minimum perpendicular to the surface. We adapted the algorithm by applying it to the ELF rather than the charge density. The resulting zero-flux ELF minima were used to partition the volume into regions belonging to each atom. These partitioned regions were then applied to the charge density, allowing the total charge for each atom to be integrated.

When applied to Ca_2N (Figure 1A), a well-studied electride, we found that the electride charge was −1.01, which is similar to the −1 formal charge that is typically assigned, $[Ca_2N]^+ e^-$, and matches the value inferred from Hall effect measurements, 1.39×10^{22} per cm^3, or 1.01 e^- per formula unit.[2] Despite this promising result, when we used this initial algorithm to partition charge across a diverse set of binary ionic compounds (N = 157), we found that the oxidation states of the atoms were consistently larger than expected. For example, in NaCl (Figure 1B), Na had a +0.97 charge, which is significantly larger than conventional values (e.g., +0.88 from Bader analysis). Although +0.97 is close to the expected formal charge of +1, the tendency of the initial algorithm to yield formal charges rather than fractional oxidation states loses valuable chemical insight.

To understand why oxidation states were overestimated relative to Bader analysis, we examined the atomic volumes that resulted from partitioning at the ELF minima. We consistently observed that cations like Na were highly spherical (Figure 1B), while the anions acquired nonspherical shapes by occupying the remaining volume. This likely occurred because anions consistently have higher ELF values than cations (e.g., Figure 1B), which systematically shifts the zero-flux surface toward the cation. This effect systematically reduced the volume of cations, decreasing their electron count and increasing their oxidation state.

The spherical shape of the cations encouraged us to examine the radii defined by the ELF minima. Interestingly, we observed that the ELF radii were close to the Shannon crystal radii, which is widely used as a benchmark.[22] For example, in NaCl (Figure 1C), partitioning along the Na−Cl bond yielded a Na radius of 1.10 Å, close to the Shannon crystal radius of 1.16 Å. Across all 157 ionic crystals, we determined both the cation and anion radii by dividing at the ELF minimum along the nearest neighbor anion−cation bond. Comparison of the ELF radii with available Shannon crystal radii revealed a nearly 1:1 agreement (Figure 1D).

https://doi.org/10.1021/jacs.3c10876
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

Because the ELF radii yielded important chemical insight, we altered our charge integration algorithm to directly use these ELF radii. We applied a Voronoi-like scheme in which atomic volumes were separated along the bonds between neighboring atoms by using a perpendicular plane located at the ELF minima. This scheme allowed the ELF radii to take a primary role in partitioning charge while simultaneously allowing both the cation and anion to adopt convex shapes. These improvements yielded charge integrations that were similar to those of the Bader method. For example, in NaCl (Figure 1E), the Na charge was +0.89, close to the Bader value of +0.88.

Because electride regions often adopt nonspherical shapes, we did not use the Voronoi-like partitioning but instead continued to partition the entire electride boundary at the ELF minima. An example of this combined partitioning scheme is shown in Figure 1F for Ca_2N, where the atoms maintain convex shapes at boundaries with other atoms, while the electride's bare electrons are allowed to fill nonspherical volumes. This combined algorithm, which uses a mixture of Bader and Voronoi partitionings, is what we introduce as the BadELF algorithm.

To benchmark BadELF versus the Bader method, we compared the oxidation states of 157 ionic crystals. These show good agreement between Bader and BadELF oxidation states, with a slope near 1 (Figure 2; see also the Supporting Information for tabulated values). The small positive *y*-intercept (+0.18) indicates a systematic tendency for BadELF to yield oxidation states that are slightly larger than Bader. Inspection of the ELFs for materials with larger BadELF values (e.g., GeTe or MnN) revealed moderate degrees of covalency, which shifted the ELF minima and increased the BadELF oxidation states. Although this highlights a limitation of the current BadELF algorithm, the differences between Bader and BadELF are small, suggesting that BadELF is a useful technique for determining oxidation states in ionic systems.

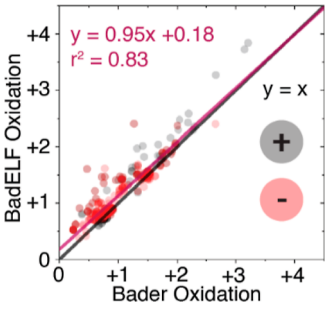


Figure 2. Comparison of conventional Bader oxidation states to BadELF oxidation states across N = 157 ionic crystals. To include anions in this plot, we have taken the absolute value of each anion's oxidation state. This plot excludes electrides.

To examine BadELF's use with electrides, we applied the algorithm to two common electride structure types: anti-$CdCl_2$[23−26] and anti-TaS_2[27] (Figure 3). The anti-$CdCl_2$ structure is the most diverse and includes widely studied metal nitrides (e.g., Ca_2N) and metal carbides (e.g., Y_2C). For the metal nitrides, the metal (Ca, Sr, and Ba) and N are widely believed to have oxidation states of +2 and −3.[10,24] Using Pauling's approach to calculate percent ionicity from electronegativity,[28] these formal oxidation states yield true charges of +1.3 (M) and −2.4 (N). Using BadELF, we instead found that

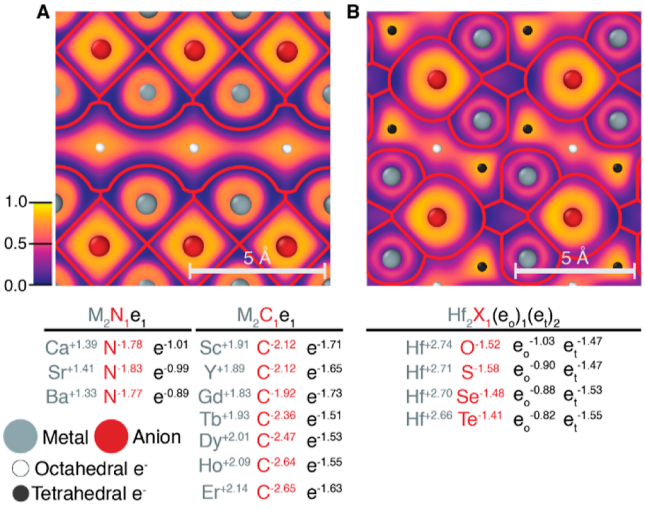


Figure 3. Partitioning scheme, oxidation states, and electron counts for (A) M_2N or M_2C and (B) Hf_2X electrides. e_o and e_t refer to local maxima in the ELF in the octahedral and tetrahedral sites, respectively.

the oxidation states for M_2N are +1.4 and −1.8 (Figure 3A). This is a considerable disagreement, but it leads us to a fascinating conclusion. Because of charge transfer from Ca to the electride state, N receives substantially fewer electrons (0.6 e^-) than expected by Pauling's approach, or, stated more provocatively, the electride receives more electrons from N (0.6 e^-) than from M (0.4 e^-). This conclusion does not conflict with Hosono's[9] or our[23] design rules that emphasize the importance of an electropositive metal in forming an electride. It does, however, highlight the essential role of the second element (here, N) in forming the electride. Indeed, this point is underscored by the fact that Ca, Sr, or Ba metal are not electrides at atmospheric pressure.[29,30]

BadELF calculations across the M_2C electrides reveal bare electron charges that fall between −1.5 and −1.7. This contrasts with that of the M_2N systems, whose charge is close to −1. The deviation from integer charges in the M_2C electrides is consistent with Hosono's[9] and our[23] prior suggestion of hybridization between the electride state and nearby metal atoms. Formally, the M_2C electrides can have up to two electrons in each electride lattice site (one spin up, the other spin down). By hybridizing with empty, low-lying d or f orbitals, the electride charge is decreased. In contrast, the M_2N materials, which contain Ca, Sr, or Ba, have fewer low-lying empty states, decreasing the opportunity for electride-atom hybridization.

We also examined Hf_2X, a fascinating family of electrides.[27] In these materials, the BadELF algorithm identified two possible electride sites in tetrahedral (ELF of ∼86) and octahedral (ELF of ∼0.66) holes (Figure 3B). If both sites are treated as electride sites, then the Hf and anion have BadELF oxidation states of +2.7 and −1.5. Interestingly, these values almost exactly match the ones estimated from Pauling's method (+2.7, −1.4) if the formal oxidation states of Hf and X were +4 and −2. This suggests that unlike the M_2N electrides, the Hf and X contribute similar amounts of charge to the electride states.

Although the BadELF method offers Bader-like chemical insight for both electrides and ionic crystals, there are important caveats. First, in an ELF plot, electride electrons

https://doi.org/10.1021/jacs.3c10876
J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

may appear to be similar to covalent or metallic bonds. One should take care to examine all of a material's features, including the ELF value, the distance of the ELF maxima from nearby atoms, and the oxidation states of the surrounding atoms. We argue that BadELF can be used to provide supporting evidence for the assignment of a material as an electride but that the best evidence will come from a careful combination of experimental and computational analysis.

CONCLUSIONS

The BadELF algorithm allows for a greater understanding of new and existing electrides by providing charges for both ions and electride electrons, giving new insight into the nature of chemical bonding in these exciting materials. With future refinements of the automatic selection of electride regions, the algorithm could be of great use in identifying possible electrides for experimental analysis and verification. Additional refinements to the BadELF algorithm could automate the analysis of covalent bonding, thereby vastly expanding the scope of its application. Finally, the algorithm could be utilized outside of the purpose of calculating oxidation states. The resemblance of the ELF radii to the Shannon crystal radii is particularly striking. The Shannon crystal radii are derived from the average behavior of an ion across many different crystals. In contrast, ELF radii are obtained by the computational analysis of a single material. This indicates that ELF radii could be used to obtain radii in materials with exotic oxidation states or coordination environments. Therefore, although BadELF is primarily designed for the analysis of electride charges, its potential extends far beyond this application.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c10876.

Additional details regarding code availability, binary structure selection, ionic character distinction, computational methods, BadELF convergence tests, and all oxidation states for ions in study (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This research was supported by the National Science Foundation under grant DMR-1905294. L.M.M. and R.C.R. acknowledge the NSF Graduate Research Fellowship (GRF) under grant DGE-1650116, J.D.S acknowledges the NSF GRF under grant DGE-1650114, and M.G.L. acknowledges the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) for their support.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Computational resources were provided, in part, by the Research Computing Center at the University of North Carolina at Chapel Hill.

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