Counting electrons in electrides

Samuel M. Weaver, Jack D. Sundberg, Connor C. Slamowitz, Becca C. Radomsky, Matt G. Lanetti, Lauren M. McRae, Scott C. Warren*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC, USA 27599

*corresponding author: sw@unc.edu

Abstract:
The wave nature of electrons makes the quantification of charge fundamentally challenging. In complex materials like electrides, this challenge is amplified by the small charge and complex shape of electride wavefunctions. For these reasons, popular integration methods such as the Bader method usually fail to assign any charge to the electron in an electride. To address this challenge, we advance an algorithm that, like the Bader method, assigns charge to an atom through the creation of a dividing surface. Unlike Bader, the dividing surface is defined not by a minimum in charge density but by a minimum in the electron localization function (ELF). We apply this method, “BadELF”, to the quantification of oxidation state in both ionic compounds and electrides. For ionic compounds, we observe that Bader and BadELF perform similarly; on electrides only BadELF yields chemically meaningful charges. We conclude that the BadELF method provides a useful strategy to identify electrides and obtain new chemical insight about their most essential property: the quantity of electrons within them.

Body:
Intro:

Society needs new materials to address outstanding challenges in energy, computation, and medicine. Among these new materials, electrides are an especially fascinating class because their unusual stoichiometries yield exceptional characteristics. The most important characteristic—their defining quality—is that electrides are so electron-rich that electrons are ejected from atomic orbitals and instead located in the interstitial space between atoms\(^1\). 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.\(^1\)-\(^4\) Despite these advances, it remains fundamentally challenging to quantify the number of electride electrons within a material.

The challenge to quantify electride electrons arises for several reasons. First, within a solid, electrons are waves and each electron wavefunction overlaps with others. Therefore, there is no universally correct approach for quantifying charge and there are many different methods depending on the purpose.\(^5\),\(^6\) Second, the electride electron density can be quite small compared to the charge density on nearby atoms. Because this density partially overlaps with nearby atoms, there is often no local minimum in the charge density that separates the atomic charge and the electride charge. The absence of a local minimum means that the most popular method for charge quantification—the Bader method\(^7\),\(^8\) does not work for most
electrides as it requires a local charge minimum to create a dividing surface. Third, the electride electron density is often unusually shaped—e.g., cylindrical or planar—compared to the spherical shape of an atom. Therefore, methods that project the charge density onto basis orbitals have not been implemented for electrides. Fourth, the electride charge is not bound to any atomic nucleus, so methods that measure atomic charge by perturbing the atom’s nucleus are not possible for electrides.

A hint of how to solve this problem appeared several decades ago, however. It was proposed to quantify the charge associated with water’s lone pairs using the electron localization function (ELF), but this proposal seems to have not been developed further. The ELF measures the probability of finding an electron of the same spin in the same region of space as a reference electron; the ELF is performed on a regular grid across 3D space, yielding a different value near an atom’s core (highly localized, ELF = 1) vs. its outer valence electrons (delocalized, ELF = 0). Interestingly, electride electrons also have high ELF values, which has historically been used to visualize the spatial distribution of electride electrons. Because the original proposal was not developed, it remains unclear whether such a method—i.e., the use of ELF to assign quantify charge—could address the long-standing challenge of charge quantification in electrides.

In this manuscript, we develop this proposed 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 electron localization function (ELF). The BadELF method segments the unit cell into non-overlapping 3D volumes then integrates the charge within each volume. To benchmark this algorithm, we compare the oxidation states obtained by the BadELF and Bader methods using a selection of ionic compounds. We find that BadELF and Bader methods yield highly similar results for these benchmarks. We then apply the BadELF

![Figure 1. A) Bader partitioning along a vector (labeled) between Na and Cl; B) Bader partitioning along a vector (labeled) between Y and an electride site; C) BadELF partitioning along a vector (labeled) between Y and an electride site; D) Schematic of the BadELF partitioning algorithm.](image-url)
method to electrides such as Ca$_2$N. 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 these fascinating materials.

**Results/Discussion:**

In Bader algorithms such as the version popularized by the Henkelman group$^{7,8}$, a hill climbing algorithm used to find local minima within the charge density of a system. These minima are then used to divide space into various partitions. For each partition, the charge density is summed and assigned to the point within the partition with the maximum charge. Finally, each local maximum is assigned to the closest atom and the partitioned charges are summed to give the final charge on each atom. This idea can be easily visualized in one dimension for typical ionic systems where it succeeds (Figure 1A), and electride systems where it fails (Figure 1B).

When applied to the ELF, this type of partitioning succeeds in efficiently separating ions and the non-spherical electride sites. However, the ELF around a typical cation is partitioned to a volume similar to that of a hard-sphere model for ionic radii. The ELF around the anion is then

![Figure 2. A) Average difference of Bader and BadELF cation radii from literature hard sphere values. B) Average difference of Bader and BadELF anion radii from literature hard sphere values; C) Comparison of Bader and BadELF oxidation states for cations in ionic compounds; D) Comparison of Bader and BadELF oxidation states for anions in ionic compounds.](image-url)
partitioned to be its respective hard-sphere volume plus any remaining space. In contrast, Bader analysis typically results in partition volumes that are much more like a soft-sphere model (Figure 2A-B). Thus, partitioning the ELF in this way results in an underestimate for cation charge and an overestimate for anion charge, but a good estimate for electride charge.

To maintain a high-quality partitioning of the electride site while improving the partitioning of the ions, we developed the BadELF algorithm. First, the Henkelman partitioning algorithm is run to obtain good electride charge results. Second, a new partitioning algorithm is run. This algorithm finds the local minimum along a line between two ions or electride sites and assigns a plane to this minimum that is perpendicular to the line. This creates polygonal regions of space that provide a more reasonable partitioning of the ions (Figure 1D). However, due to the irregular shape of electride sites, this algorithm typically cuts off part of the charge of the electride site and applies it to the cation. Finally, the difference between the two electride charges is applied to the closest cation.

To explore the validity of BadELF, we ran it on several ionic character materials. The resulting oxidation states are compared with those found by running Bader on the same set of materials (Figure 2C-D). We find that BadELF typically gives values that are slightly larger than Bader, but the two are generally quite close. To test BadELF’s ability to provide electron counts for electrides, we ran it on several well-studied electride systems. The resulting charges are summarized in Table 1. Bader results are left out as in all cases it provided an electride charge at or close to 0. We find that the electron charge tends towards either -1 or -1.6, which we associate with 1 and 2 electrons respectively.

<table>
<thead>
<tr>
<th>Electride</th>
<th>Electron charge</th>
<th>Metal charge</th>
<th>Anion charge</th>
</tr>
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<tbody>
<tr>
<td>Y₂C</td>
<td>-1.66</td>
<td>+2.11</td>
<td>-2.13</td>
</tr>
<tr>
<td>Ho₂C</td>
<td>-1.62</td>
<td>+2.30</td>
<td>-2.54</td>
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<tr>
<td>Er₂C</td>
<td>-1.66</td>
<td>+2.41</td>
<td>-2.69</td>
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<td>Sc₂C</td>
<td>-1.55</td>
<td>+1.93</td>
<td>-1.94</td>
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<tr>
<td>Dy₂C</td>
<td>-1.6</td>
<td>+2.24</td>
<td>-2.42</td>
</tr>
<tr>
<td>Tb₂C</td>
<td>-1.56</td>
<td>+2.15</td>
<td>-2.31</td>
</tr>
<tr>
<td>Sr₂N</td>
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<td>-1.82</td>
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<tr>
<td>Ca₂N</td>
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<td>+1.49</td>
<td>-1.79</td>
</tr>
<tr>
<td>Ba₂N</td>
<td>-0.97</td>
<td>+1.52</td>
<td>-1.77</td>
</tr>
</tbody>
</table>
Conclusion:

We have designed and demonstrated a new method, BadELF, for partitioning electrons in crystalline materials. We have shown that this method behaves similarly to Bader analysis for ionic systems, while providing reasonable results for electrides. We expect that the ability to quantify electrons using an automated algorithm will facilitate straightforward identification and high-throughput identification of electrides in the future.

References: