On the Electride Nature of Na-hP4

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In memoriam of Neil Ashcroft, who died in March 2021.

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Abstract

Early quantum mechanical models suggested that pressure drives solids towards free-electron metal behavior where the ions are locked into simple close-packed structures. The prediction and subsequent discovery of high-pressure electrides (HPEs), compounds assuming open structures where the valence electrons are localized in interstitial voids, required a paradigm shift. Our quantum chemical calculations on the iconic insulating Na-hP4 HPE show that increasing density causes a 3s → 3pd electronic transition due to Coulomb repulsion between the 1s2s and 3s states, and orthogonality of the 3pd states to the core. The large lobes of the resulting Na-pd hybrid orbitals point towards the center of an 11-membered penta-capped trigonal prism and overlap constructively, forming multi-centered bonds, which are responsible for the emergence of the interstitial charge localization in Na-hP4. These multi-centered bonds facilitate the increased density of this phase, which is key for its stabilization under pressure.

In their classic paper *On the Constitution of Sodium at Higher Densities*, Neaton and Ashcroft[1] showed that the nearly-free-electron model of Wigner and Seitz[2] was valid only at ambient or near-ambient pressures. At higher densities the effects of Pauli exclusion and orthogonality, coupled with a 3s → 3pd transition (Figure 1), stabilized low-coordinated structures whose electron density was localized in interstitial regions, heralding the onset of a metal-to-insulator transition. Almost a full decade later this intuitive prediction was verified by experiments that characterized the Na-hP4 phase.[3] First principles calculations yielded a band gap of ~1.3 eV at 200 GPa for this newly discovered allotrope, whose electronic structure was reminiscent of an electride – a compound where electrons localized at interstitial sites assume the roles of anions, and, in sodium, the ionic cores play the role of cations. Since then, many experimental and theoretical studies have tried to answer the question: "Will every element turn into an electride when squeezed?"[4,5] Herein, detailed quantum chemical calculations are performed on Na-hP4 as a model for a HPE, addressing long-standing questions regarding the emergence of the electride state under pressure.

Chemists have known of electrides since Humphry Davy's experiments on alkali metals in ammonia solutions in the 19th century.[6] The seminal work of Dye in the 1980s inspired rigorous studies of molecular electrides,[7,8] culminating in the X-ray assisted visualization of the residual electron density of an organometallic electride.[9] Examples of ambient-pressure inorganic crystalline electrides include $[Ca_{24}Al_{28}O_{68}]^{4+}[4e^-]$[10] and several layered materials,[11] some possessing industrially-useful catalytic properties.[12] Theoretical calculations predict that in addition to alkali and alkaline earth metals,[13,14] aluminum[4] and carbon,[5] even exotic compounds like Na_2He[15] can become electrides when squeezed, suggesting that at high pressure the electride state may actually be quite common.

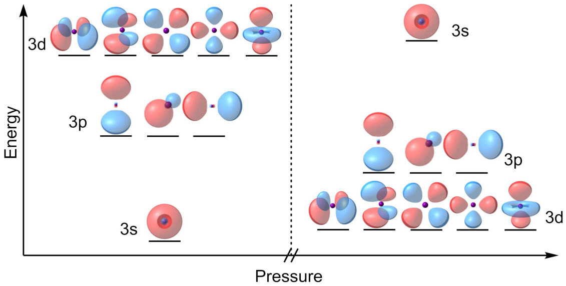

Figure 1. Schematic illustrating the concept of energy-level reorganization upon compression for an isolated atom of sodium, based on the expected Coulomb repulsion exerted by the core, resulting in 3s → 3p and 3p → 3d electronic transitions. Though interatomic interactions in the solid state may affect the orbital ordering, it will still differ significantly from the orbital ordering found at ambient conditions.

Theoretically, electrides can be characterized using several electron density (ρ) based methods,[16,17] such as the Quantum theory of Atoms in Molecules (QTAIM), as well as Electron Localization Functions (ELFs) and Non-Covalent Interaction analyses. As suggested from studies on molecular systems,[17] an electride should fulfill at least three topological criteria and possess: 1) a non-nuclear attractor (NNA, local maxima of the electron density that does not coincide with an atomic position), 2) negative value of $\nabla^2\rho$ at the NNA position (meaning that charge accumulates at that position), and 3) the presence of an ELF basin. The NNA lends some kind of identity to the electride, with an unambiguous physics definition for its volume and charge.[18] Even though this characterization appears to be quite straightforward, there is, to date, no theory that can unequivocally explain and predict HPE formation. The most thorough attempt thus far is the theory of Interstitial Quasi-atoms (ISQs) by Miao and Hoffmann.[19,20] If the energies of orbitals centered on interstitial sites devoid of an atomic nucleus, which possess s orbital character, become lower than the energies of atom-centered orbitals upon densification, ISQ theory predicts that electrons will move off the atoms to the interstitial regions forming a HPE. Calculations on lithium and sodium atoms confined in a pressure-simulating helium matrix corroborate this theory.[19]

Though ISQ-theory is chemically appealing it does not explain HPE formation in all elements, and the original calculations, which were carried out over a decade ago, at times lack predictive power. For example, it has long been hypothesized that elements such as Ca[21] and Cs[22,23] become electrides because their valence electrons undergo pressure induced s → d transitions. Moreover, though ISQ theory predicts that Tl becomes a HPE[19], calculations on experimentally observed structures suggest that pressure induced sp→d transitions, not considered by Miao and Hoffmann for this element, inhibit the formation of the electride state.[24] Finally, though some ambient pressure phases of pure metals, including Sc and Al together with alkali and alkaline earth metals,[25,26] and even gas-phase clusters of sodium and lithium[18,27,28] possess charge localization loci (corresponding to NNAs) and all the topological requirements to be classified as electrides, they would not necessarily be predicted as such by ISQ-theory. In fact, charge concentrations in interstitial regions in electropositive metals are traditionally attributed to the formation of metallic bonds, and not to electride formation.[25,26] Therefore, it seems that further investigations are still necessary to understand the forces driving the formation of HPEs.

Na-hP4 is one of the most extensively characterized HPEs,[3,14,29,30] being simple in structure, chemical composition, and relatively easy to form upon compression (by ~200 GPa in a diamond anvil cell). Surprisingly, there is no general consensus as to why Na-hP4 becomes an electride. In addition to the aforementioned combined effects of Pauli exclusion, Coulomb repulsion and orthogonality,[1] and the ISQ-theory,[19,31] the proposed mechanisms include: repulsions due to core exclusion,[32] and valence s-p[29] or p-d hybridizations.[1,3,14,30] Herein, we present the results of careful quantum chemical computations designed to answer the following questions for Na-hP4. i) What are the orbitals responsible for the formation of the electride state? ii) What is the role of the core-electrons? And iii) Are the localized electrons best described as those centered on ISQs, or do they still belong to the surrounding atoms, being manifestations of the build-up of electron density arising from multi-centered chemical bonds?

To answer these questions, density functional theory calculations were performed using the HSE06 functional, coupled with either planewave or atom centered basis-sets on the experimental Na-hP4 geometry at select pressures[3] (Section S1). Projection of the electronic band structure onto localized orbitals is the most obvious approach to answer the first question. However, care must be taken in performing such an analysis to avoid inaccurate projections (Figure S1-S3). The planewave based codes used by us and others, associate to each atom a spherical volume that encloses the projection onto fixed atomic orbitals, and therefore they only have a qualitative meaning. Using the default parameters provided in one of the most popular band structure programs, VASP, such calculations generally suggest that the valence states of Na-hP4 exhibit primarily Na s[20,31] or hybrid s-p character.[29] However, these results are sensitive to the size of the projection's sphere. Unless the spheres perfectly cover the entire space of the unit cell without overlapping with each other - an impossible task in Na-hP4 due to the presence of the cavities - the projection cannot be complete (Section S2). Optimization of the sphere size based on a Bader analysis, or by choosing spheres whose volumetric sum is the same as the total volume of the cell suggests various degrees of s-p-d hybridization instead (Figure S2).

When localized basis functions are employed, the electronic states are projected on the very same orbitals used to generate the band structure. Moreover, it becomes possible to add or remove orbitals from the basis, enabling studies that consider how the presence or absence of specific functions affects the electronic structure of a compound. Therefore, we constructed an optimized basis (named *Na*) containing all core states, as well as sodium 3spd functions that yielded the density of states, band gap, ELF, topology of the electron density, and NNA charges that agreed with the results of planewave codes (Figure 2, Table 1). Removing the 3d (*Na-d*) or 3pd (*Na-pd*) functions from the basis restricts Na to adopt either a 3sp or 3s electronic configuration, predicting metallic behavior for Na-hP4, sided by the disappearance of the charge concentrations in the cavities. This is shown most clearly when the ELF obtained from the *Na-d* basis is subtracted from that obtained with the optimized basis (Figure 2b). Adding a single s (*Na-pd+1s*) function, or three s functions with different orbital exponents (*Na-pd+3s*) in the interstitial regions treats Na as having a 3s^1 configuration, but it allows the possibility for electrons to be transferred to ISQ-like orbitals. These basis sets yielded band gaps that were too large (2.5-2.9 eV), and ELFs that were too localized (*e.g.*, Figure 2c). Adding back the p functions to both basis-sets (*Na-d+1s* or *Na-d+3s*), yielded band gaps that were somewhat smaller than expected (0.8-1.2 eV), but not unreasonable, and ELF plots that even resembled the planewaves results (Figure S4).

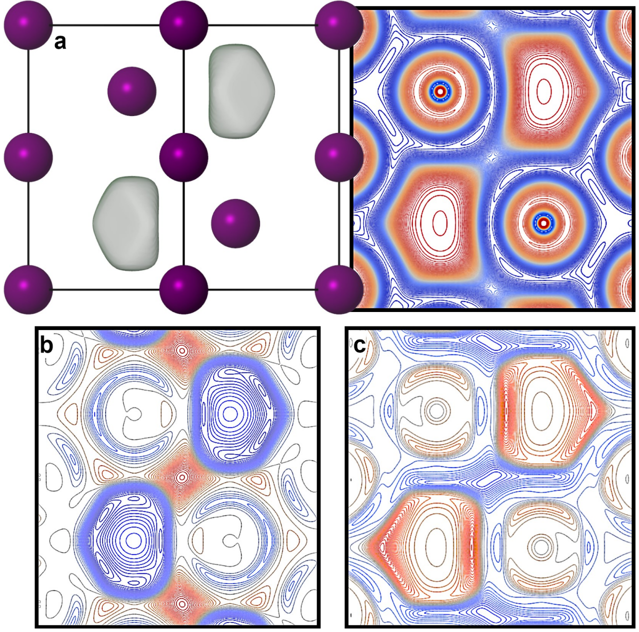

Figure 2. a) 3-D ELF basin (isovalue = 0.8) and 2-D plots along the (110) plane of Na-hP4 at 190 GPa (*Na* basis set). 2-D ELF difference calculated between the b) [*Na-d* – *Na*]; c) [*Na-pd+1s* – *Na*] basis sets. The color scale in the 2-D plot of (a) goes from 0 (blue) to 1 (red), while in (b) and (c) it goes from -0.25 (blue) to +0.25 (red).

ELF provides a visual and qualitative analysis of the electronic structure. Could a quantitative measure be used instead? A feature of the electron density characteristic only of electrides[17] and some pure metallic bonds,[25] is the presence of NNAs at the center of the ELF's lobes. Therefore, to unambiguously distinguish between the atom-centered basis-sets that could potentially describe the electronic structure of Na-hp4 (*Na*, *Na-d+1s* and *Na-d+3s*) we analyzed the topological features of the NNAs, *i.e.*, electron density (ρ) and Laplacian of the electron density ($\nabla^2\rho$), by means of QTAIM. As show in Table 1 and Figure S4, an electron density topology that agreed with the planewave results could only be achieved when the electrons in the cavities were generated via sodium pd hybrids as in the optimized *Na* basis. If ISQ centered s-orbitals were employed instead, the electron densities in the cavities were too localized (with large absolute values of ρ_{NNA} and $\nabla^2\rho_{NNA}$).

Table 1. Band gaps [eV], values of electron density (ρ_{NNA}) [e/bohr^3] and its Laplacian ($\nabla^2\rho_{NNA}$) [e/bohr^5], integrated charge (q_{NNA}) [e] at the NNA positions calculated with atomic-orbital (AO) and plane-wave (PW) basis sets (HSE06 functional). The number of valence electrons used explicitly in the plane-wave calculations is provided.

Basis-set (AO)	**Band-Gap**	ρ_{NNA}	$\nabla^2\rho_{NNA}$	q_{NNA}
Na	1.25	0.048	-0.035	-1.10
Na-d	0.00 (metallic)	N/A	N/A	N/A
Na-d+1s	0.78	0.061	-0.100	-1.14
Na-d+3s	1.19	0.057	-0.763	-1.14
Na-pd	0.00 (metallic)	N/A	N/A	N/A
Na-pd+1s	2.50	0.077	-0.159	-1.20
Na-pd+3s	2.92	0.062	-0.862	-1.15

Valence Electrons (PW)	**Band-Gap**	ρ_{NNA}	$\nabla^2\rho_{NNA}$	q_{NNA}
9	1.23	0.049	-0.043	-1.08
7	1.24	0.049	-0.042	-1.07
1	1.25	0.051	-0.047	-1.02

Therefore, the most appropriate way to view the valence electronic states of Na-hp4 is as 3pd hybrids, and any extra functions at the ISQ sites need not be invoked, in-line with Neaton and Ashcroft's original thesis. Upon densification, the Na 3s orbitals experience repulsion from the core, but the 3p and 3d do not because of orthogonality. This effect, quantified through an analysis of the intra-atomic Crystal Orbital Overlap / Hamilton Populations (Table S3) is responsible for the pd hybridization, but it does not imply that the valence pd-electrons are expelled from the atom into the ISQ sites. To test whether the 2s and 2p orbitals affect the electronic structure of Na-hP4, either by polarizing or by repelling the outermost electron, additional planewave calculations were performed explicitly treating either 7 or 1 valence electron. The band gaps and topological descriptors obtained did not depend upon the number of valence electrons considered (Tables 1, S1-S2). Finally, our QTAIM analysis (Table 1) located NNAs inside the cavities of Na-hP4, characterized by negative Laplacians and ELF lobes, so the aforementioned electride-state-checklist is fulfilled.[17]

To better understand how such Na pd hybrids yield the electron density calculated for Na-hp4, we constructed a Wannier-like function (WF)[33] that exactly reproduced the doubly occupied valence band of this allotrope (Figure 3a). A constructive overlap of pd hybrids placed on a square lattice yields an A1$_g$ molecular orbital with a build-up of electron density in the interstitial (Figure 3b/3c). Analogously, the NNA-centered WF in Na-hP4, which clearly resembles the ELF feature associated with the localized electron, results from an "in-phase" overlap of pd hybrids on 11 Na atoms. This WF is therefore a consequence of a multi-centered bond formed within a penta-capped trigonal prism whose nearest neighbor Na-Na distances vary from 1.995 to 2.920 Å at 190 GPa, with the distance to the center of the cavity ranging from 1.686 to 2.135 Å. The concentration of electron density in the cavities allows Na atoms to be closer to each other resulting in a decreased volume, which is the reason why Na-hP4 becomes more stable than bcc under pressure (Section S6). The integrated Bader charge within the NNA, approx. 1e, resembles calculations performed for analogous systems,[27] and the rest of the electron density, shared within the framework, accounts for the smaller lobes of the hybrid orbitals. A picture where the charge density within the cavity results from multi-centered bond formation, and the rest is distributed around the Na atoms in the framework, is a less ionic situation then a doubly occupied localized ISQ, and more in line with the semi-conducting band-gap of ~1.3 eV (Table 1).

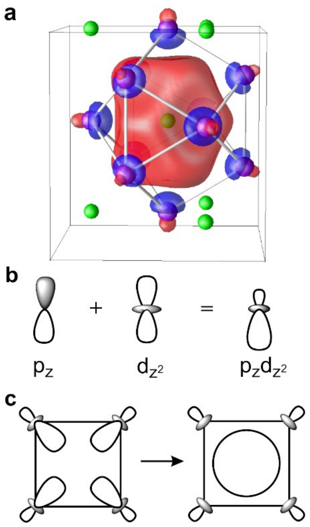

Figure 3. a) The NNA-centered Wannier-like function that describes the valence band in Na-hP4 at 320 GPa. Na atoms /NNAs are purple/green. Schematic of b) p_z and d_{z2} orbital hybridization; c) a multicentered bond formed from pd hybrids pointing towards the square's interior, resulting in a cavity-centered molecular orbital.

Interestingly, QTAIM identifies the localized electrons within this HPE as well-defined topological entities connected with the Na atoms (Figure S6-S7, Table S4). Although "topologically connected" does not necessarily mean "chemically bonded", the presence of NNAs, and their contacts with the surrounding atoms, is an intrinsic characteristic of several metallic compounds, naturally emerging upon formation of chemical bonds.[26] In fact, NNAs, and the familiar ELF blobs associated with the electride state, are not a consequence of pressure either, but they exist in gas-phase,[18,26,27] as well as in solid state compounds at ambient conditions.[25] Moreover, the presence of NNAs in cavities, like in Na-hP4, instead of in-between atoms, is again a consequence of the electronic transition to (p)d-orbitals, which provide the extra directionality off the interatomic axes (Section S7). In fact, removing the (p)d-orbitals from Na (Figure 2, S4b), led the charge concentrations in the cavities to disappear. Therefore, we conclude that electrides like Na-hP4, and many others involving electropositive elements[9,25] can be described by means of (multicentered) chemical bonding schemes, which might become ubiquitous under pressure.[34]

Thus, we have obtained the following answers to the questions posed above: i) atom-centered pd-hybrid orbitals whose overlap leads to charge concentrations in the cavities define the electride state in Na-hP4; ii) the only effect of sodium's core upon densification is to hasten the electronic 3s→3pd transition, but it plays no role in the generation of the electride state associable with "squeezing out" electrons from the atom; iii) the electrons in the cavities of Na-hP4 are not unbound, isolated objects, but they are generated by the sharing of the electron density of the surrounding sodium atoms, forming exceptional multicenter-bonds.

By considering all of the theories proposed for the formation of the electride state in high-pressure systems,[1,3,19,29,32] we illustrated conclusively that the arguments of Neaton and Ashcroft are the only valid quantum mechanical explanation for the emergence of this state in compressed Na, which behaves similar to K, Rb and Cs under pressure. However, our work goes beyond the physics picture painted by Neaton and Ashcroft, connecting it with chemical concepts of bonding. Specifically, we show that a Wannier-like function that spans the valence bands of Na-hP4 can be interpreted as pd hybrid orbitals that overlap in a constructive way in the interstitial region where the excess electron is found, as in a multi-centered chemical bond. The sharing of electrons inside a cavity within an Na_{11} cluster, instead of along a nearest-neighbor contact as in a two-center chemical bond, is in fact a consequence of the hybridization between orbitals of higher angular momentum, here *p* and *d*, that confer extra dimensionality to the interatomic interactions. The analysis presented herein is the first step towards a predictive theory for the discovery of solid-state electrides based upon crystal structure prediction methods and QTAIM descriptors.

Acknowledgements

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Keywords: Electride • High Pressure • Sodium • Alkali metals • Chemical Bonding

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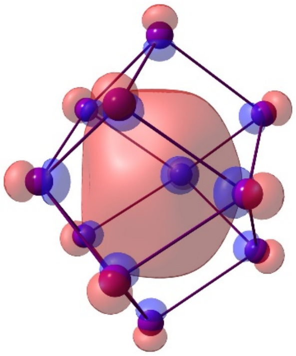

The Na-hP4 phase, a high pressure electride, contains clusters of eleven sodium atoms within which charge is localized. Quantum chemical calculations show that this build-up of interstitial charge stems from the overlap of pd hybrid orbitals on the sodium atoms comprising this cluster, resulting in the formation of a multi-centered bond, increased density, and semiconducting behavior.

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