

High Pressure Electrides: A Predictive Chemical and Physical Theory

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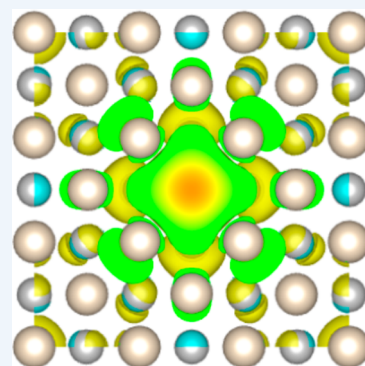
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Supporting Information

CONSPECTUS: Electrides, in which electrons occupy interstitial regions in the crystal and behave as anions, appear as new phases for many elements (and compounds) under high pressure. We propose a unified theory of high pressure electrides (HPEs) by treating electrons in the interstitial sites as filling the quantized orbitals of the interstitial space enclosed by the surrounding atom cores, generating what we call an interstitial quasi-atom, ISQ.

With increasing pressure, the energies of the valence orbitals of atoms increase more significantly than the ISQ levels, due to repulsion, exclusion by the atom cores, effectively giving the valence electrons less room in which to move. At a high enough pressure, which depends on the element and its orbitals, the frontier atomic electron may become higher in energy than the ISQ, resulting in electron transfer to the interstitial space and the formation of an HPE.

By using a He lattice model to compress (with minimal orbital interaction at moderate pressures between the surrounding He and the contained atoms or molecules) atoms and an interstitial space, we are able to semiquantitatively explain and predict the propensity of various elements to form HPEs. The slopes in energy of various orbitals with pressure ($s > p > d$) are essential for identifying trends across the entire Periodic Table. We predict that the elements forming HPEs under 500 GPa will be Li, Na (both already known to do so), Al, and, near the high end of this pressure range, Mg, Si, Tl, In, and Pb. Ferromagnetic electrides for the heavier alkali metals, suggested by Pickard and Needs, potentially compete with transformation to d-group metals.



INTRODUCTION

Though we would like electrons to be attached to nuclei in atoms or ions, or to be shared between them, there is a body of $P = 1$ atm knowledge (not easily won) of electrons in interstitial sites, electrides, stabilized by the surrounding atoms. Our concentration on high pressure electrides (HPEs) leaves us in despair here at not being able to discuss the beautiful work of Jim Dye on ambient pressure electrides.^{1,2} Nor the 200-year-old history of metal-ammonia solutions.^{3–5} Nor the remarkable alkali metal suboxides,⁶ as well as other ambient condition electrides.^{7–9} The Supporting Information (SI) to this paper contains more references.

One might have thought there would be fewer nooks and crannies for electrons in dense matter under high pressure. Apparently not so. Electrides have been experimentally observed and theoretically calculated in a variety of high pressure phases of simple metals. Electron density in the interstitial sites of pressurized elemental structures was first predicted for Ca,¹⁰ Li,¹¹ and Cs.¹² Experimental observations and theoretical calculations for Li^{13–17} and Na^{18–22} followed. Both crystallize in the body centered cubic (BCC) structure at 1 atm and transform into a face centered cubic (FCC) structure under moderate pressure. At higher pressure, the alkali metals leave their close packed atomic arrangements for denser, yet lower symmetry structures. Yet these geometries contain

seemingly empty sites, not spacious, but as large as the atoms/ions; calculations reveal electron density residing in these supposed “voids.” The electronic consequences are staggering: starting at ~ 120 GPa, the experimental IR and visible reflectivity of Na drops, as does its plasma frequency. The element becomes transparent to visible light, consistent with a sizable band gap calculated.^{19–22} The first explicit suggestion that the unusual high pressure phases are to be viewed as electrides is due to Y. Ma and coworkers;¹⁹ the idea is clearly there also in the work of E. G. Maksimov, M. G. Magnitskaya, and V. E. Fortov.²³

Computational work points to possible HPE formation in elements beyond the alkali metals: in Al at 5 terapascals (TPa),²⁴ Mg at 800 GPa,²⁵ and C at 25 TPa.²⁶ The HPE phenomena is observed or predicted in compounds as well as elements. These are as diverse as Mg₃O₂, Na₂He, and Li(NH₃)₄; the relevant citations are given in the Supporting Information (SI) to this paper.

In an important guidepost to us, Rousseau and Ashcroft²⁷ constructed a model for high pressure interstitials which featured a system of noninteracting electrons moving in the variably configured space of an array of periodically disposed

Received: December 5, 2013

Published: April 5, 2014

(FCC, simple hexagonal (SH)) impenetrable spheres. Here we explore a related model, one in which exclusion from a region of space and confinement also figure crucially. In our model, we use a helium lattice as a confinement medium, both of space for an electron, and for an atom of a potential HPE-forming element. What we observe in detailed calculations can be well understood on the basis of another model, an electron confined by a spherical bounding surface. The outcome is a chemical and physical picture of the HPEs, one with predictive features across the Periodic Table.

■ WHY HIGH PRESSURE ELECTRIDES FORM

We will term the confined space between atoms, a space that can be potentially occupied by an electron, together with that electron, an interstitial quasi-atom (ISQ).²⁸ This space is not necessarily spherical, of course, though one might in a first approximation model it as such.

Suppose the size of an ISQ is comparable to that of an atom at a given pressure. Figure 1, right plots schematically the

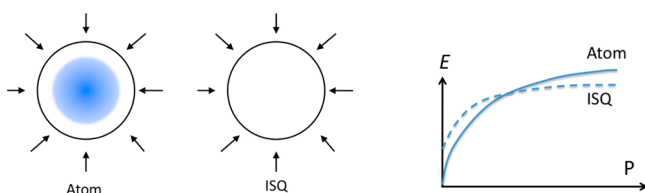


Figure 1. (left) Cartoon of a compressed atomic core versus an ISQ. (right) Schematic enthalpy of adding an electron to an atomic core versus placing it in an ISQ as a function of pressure.

energy of adding an electron to an underlying ion versus adding it to an ISQ; Figure 1, left shows even more schematically an ion A^+ (say Na^+) and the ISQ, modeled by a sphere. Of course, the energy levels of each, A^+ and ISQ, each with an electron, rise with increasing pressure. At some characteristic radius (whose inverse cube scales roughly with the density, and therefore the imposed pressure), it will cost more enthalpically to place an electron on the ion than in the ISQ. This is because A^+ has other electrons there, in its core, and any added electron, even as it is attracted to the core, has to remain orthogonal to the core electrons. One could think that the electron has less effective space available to it when it is added to A^+ , compared to it being placed in an ISQ of similar size. Less space for electronic motion implies higher energy.

■ A HELIUM CONTAINMENT MODEL FOR AN ISQ

To proceed further, we need a model for the relative energy levels of an ISQ and an atom. For this purpose, we take advantage of the relative chemical inertness of the noble gases. We begin with an FCC lattice of He atoms, the most unreactive of these, and calculate its lattice constants under pressure from 0 to 500 GPa. We then take a $(3 \times 3 \times 3)$ supercell of the nonprimitive cubic cell of this structure, containing 108 He atoms, and replace one He in the supercell with an atom under study, A, or simply remove one central He to create an empty space (the ISQ model). We then relax the positions of all atoms, but at the same time keep the lattice constants of the supercell. The restriction to $P < 500$ GPa is because as inert as we imagine He to be, at higher pressures, one does get significant orbital interaction between the atom and ISQ on one hand and He 1s and 2s/2p orbitals on the other.²⁹ By examining the wave functions, we can identify the A or ISQ

orbitals, and follow their energy as a function of pressure. The theoretical methodology used is described in detail in the SI to this paper; it consists essentially of plane-wave-based DFT calculations of the model.

In optimizing the 107 atom He model for the ISQ ($3 \times 3 \times 3$ FCC supercell minus one He), we maintain the point group symmetry (O_h). This prevents the central vacancy from being obliterated, for the neighboring 12 He's all have to move together as pressure is applied. The ISQ center to neighboring He distance at 500 GPa comes out to be only 0.04 Å shorter than the He–He distance of 1.39 Å in the unperturbed He lattice at this pressure.³⁰ And whether one adds one electron to the ISQ model or keeps it neutral causes almost no change to the geometry of the array at higher pressures.³¹ Figure 2 shows

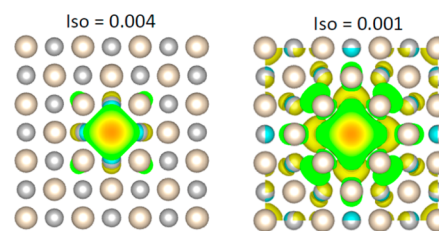


Figure 2. Electron density for one electron in the ISQ 1s orbital in an FCC He lattice 107-atom model. Here two values (indicated) of the electron density (in electrons/bohr³) are chosen, and the color indicates the magnitude of electron density values exceeding the isosurface.

a plot of the electron density for an electron in the lowest energy orbital of the ISQ as modeled by a vacancy in a helium lattice. Notice the relatively small, but noticeable departure from spherical symmetry.

■ ANOTHER MODEL FOR AN ISQ, AN ELECTRON WITHIN A SPHERICAL BOUNDING SURFACE

There is another way to approach modeling the interstitial space that is potentially available to electrons under high pressure; this is by the simplest quantum mechanical model of an electron(s) constrained to move within a spherical bounding surface. We were led to this model by thinking of the potential an electron feels if it were localized in an interstitial space. Staying with the He model outlined above, to estimate the potential, we need the energy of an electron interacting with a He atom; this potential has long been of interest in the context of electrons in liquid or solid He.³² If one plots (see SI) the energy of an electron moving out of the center of the computed ISQ cavity toward a confining He, or toward the largest “hole” of the surrounding first-coordination sphere of 12-cube-octahedrally disposed He atoms, one obtains a deep well. The well is pretty harmonic and about 6 eV deep over a range of pressures.

We could model the above potential by a spherical harmonic oscillator (it can be fitted by a harmonic potential with a small quadratic contribution), a model much explored in the shell model of the nucleus.³³ We opt for an even simpler choice, the spherical container with zero potential inside, infinite walls at radius R . The simplicity of this textbook problem is matched by its utility: witness its use, in various incarnations, with walls and floor tinkered with, for magic electron counts in atomic clusters,³⁴ and for the solvated electron in metal–ammonia solutions.³⁵

The wave functions of this familiar problem³⁶ are spherical Bessel functions, and the energy levels can be expressed as

$$E(n, l) = z_{n,l}^2 \frac{\hbar^2}{2mR^2} \quad (1)$$

in which n and l are the principal and angular momentum quantum numbers, R is the ISQ radius (as we noted, a realistic ISQ may not be spherical, of course, but is here modeled as such), and $z_{n,l}$ are dimensionless constants, the zeros of the Bessel functions characteristic of the problem. The energy level ordering of this archetypical explicitly soluble problem is 1s below 1p below 1d below 2s, and so forth, independent of the size of the box; the levels are shown in the SI for one value of R . The fact that p and d levels come below 2s in this model is going to be physically significant in the sequel.

How does the He vacancy model for the ISQ compare to the particle confined by a spherical bounding surface? Figure 3

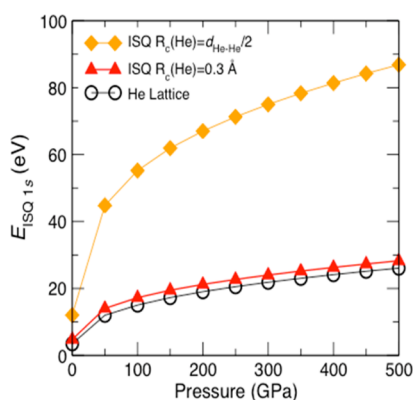


Figure 3. Comparing the 1s orbital energies from FCC He model with the particle in a box model at various assumed values of the radius of the containing sphere, $R = D_0 - R_c$. For the orange line, the radius reduction R_c is taken as the half of the He–He distance in FCC. The red line is the best fit to the actual ISQ calculations, $R_c = 0.3 \text{ \AA}$.

shows in open circles the energy of the ISQ He model for one electron in the ISQ. To compare with an electron confined in a spherical volume with infinite walls, we need to specify the model radius R . How to estimate R ? Suppose we define $R = D_0 - R_c$ where D_0 is the distance between the center of the ISQ and the nearest He nucleus in the relaxed 107 atom model of the ISQ and R_c is a radius reduction. A zeroth order estimate of the radius reduction (effectively the specification of an effective excluded volume) might be the radius appropriate to a He atom at the specified pressure. This may be estimated by taking one-half of the He–He separation in the unperturbed He lattice, the 108 atom model. That separation ranges from 2.873 Å at $P = 0.001 \text{ GPa}$ to 1.390 Å at $P = 500 \text{ GPa}$. The resulting energies (top curve in Figure 3) rise too steeply. The effective radius must be larger, for (as Figure 2 showed) the ISQ is moderately nonspherical and penetrates somewhat into the region between the surrounding He atoms. Alternatively, we can estimate an effective He radius reduction by fitting to the calculated potential. As we can see from Figure 3, R_c of 0.3 Å gives a good match between the He model and the particle in a spherical container levels for the ISQ.

As we will see, the particle in a potential free container model shares an important feature with another model essential for understanding HPEs, that of a Coulombic system in a confined

space. This feature is that compression of an atom raises in energy orbitals with angular nodes less than those radial ones.

■ USING THE He CONFINEMENT MODEL TO DECIDE WHICH ELEMENTS MIGHT FORM HPEs

To probe the propensity of forming HPEs, to begin, we examine the group 1, 2, and 13 elements of the first two periods. The lower periods in Mendeleev's Table present a special situation, to which we will return. We replace one helium out of 108 by a "heteroatom," and plot the resulting energies of the least strongly bound or frontier electron of that heteroatom, in its s or p or d orbital, relative to the energy of the ISQ model, in Figure 4. A positive energy indicates that the orbital in question would transfer its electrons to the ISQ at the pressure indicated.

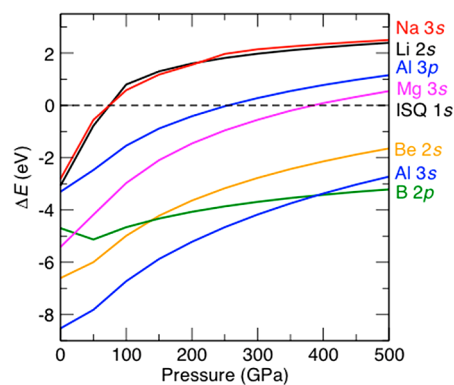


Figure 4. Orbital energies (in the helium containment model) of an electron in the highest occupied orbital of selected Group 1, 2, and 13 elements, referenced to the energy of an electron in the 1s orbital of an interstitial quasi-atom (horizontal dashed reference line). Positive ΔE means an ISQ will form.

This rough model captures much of the fundamental physics of HPEs. As shown in Figure 4, Li and Na have the keenest propensity to lose their electrons to the ISQ, followed by Al and Mg. This is in rough agreement with the experimental and theoretical findings in the literature. From experimental measurements, one does not obtain a direct measure of electronegativity as a function of pressure; the observable consequences are a diminution or loss of metallic conductivity, an approach to optical transparency, changes in static dielectric constant, and the development of plasmon frequencies. Theory has an easier time of pointing to electronegativity through electron density and electron localization function (ELF) plots. Both theory and experiment point to electronegativity formation in Li and Na in the 50–80 GPa range,^{11,13–23} where our simple model predicts it. There is as yet no evidence for Mg and Al electronegativity at moderate pressure, 250–400 GPa. But at higher pressure, electronegativity behavior was predicted for Al²⁴ and Mg.²⁵

The general trend shown in Figure 4 also makes sense. As a first approximation, the pressure at which a given element's frontier electron (electron easiest ionized) shifts to the ISQ should correlate with the first ionization potential (IP) of the element; the lower the IP, the easier should transfer of an electron to an ISQ be. Thus, Mg should become an HPE at substantially higher pressure than Li or Na. And Be, which has a still higher IP, is not likely to form a HPE until very high pressures. Note the parallel pressure dependence for these four s-block elements.

p-Block elements introduce a different pressure dependence. So Al has about the same IP as Na, but its frontier electrons cross the ISQ energy only at substantially higher pressure. As the computed slopes indicate, this is because the valence 3p electrons of Al are less sensitive to pressure than s-orbital electrons.³⁷ The behavior of the energy of the frontier B 2p electron is very different; note its almost flat variation with pressure (we will return to the reasons for this). The major difference between B and Al is that the latter has an inner shell p orbital, 2p, which acts to effectively prevent the penetration of 3p electrons into the core region. B has a 1s core, but no inner p orbital.

The reader will note that group 1 and 2 metals, K, Ca, and lower, are not in Figure 4. These are special cases, for in them the frontier orbitals behave as shown in Figure 5. They do have

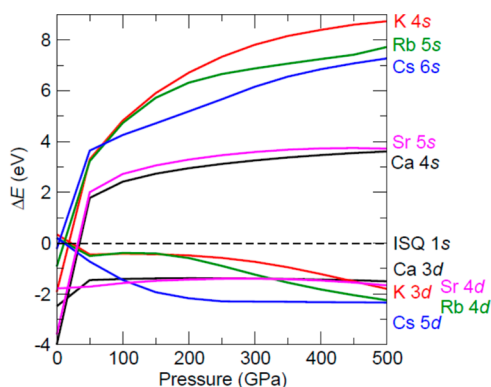


Figure 5. Effect of d orbitals in forming HPEs for selected alkali metal and alkaline earth metal atoms.

low ionization potentials. And their ns electron energies indeed rise rapidly under pressure, as they did for Li and Mg. But in the third period of the Periodic Table, and below, one has not far above the ns level that is singly or doubly occupied in the atom, an $(n - 1)d$ level. That level, unoccupied at $P = 1$ atm, actually falls in energy initially (compared to the ISQ reference; on an absolute scale it rises) as a function of pressure, as Figure 5 shows. Thus, the frontier electrons essentially switch under pressure from being ns to $(n - 1)d$, a phenomenon well-studied for K³⁸ and Ca,²³ as well as for other alkali metals.³⁹ Electride formation as well as d-orbital occupation, has been predicted for Ca at moderate pressures.^{10,23,40} We will return to the history and the reasons for the s–d switch below.

In an important paper, Pickard and Needs find that K and the heavier alkali metals can form at relatively low pressures (near 20 GPa) quite unusual s-band electrides, stabilized by ferromagnetic ordering.⁴¹ In the case of K, the prediction is that a ferromagnetic electride phase may be more stable than the d-band metal. Our model does not have magnetism in it at this stage; with the Pickard and Needs result accepted at face value, all we can say is that in the heavier alkalis one will under pressure either switch the outermost s electron to a d level, or form an electride.

We next looked at some other main group elements, in Groups 13–17. The results are shown in Figure 6. Note the difference between C and Si, analogous to the B/Al differences mentioned above: the C 2p does not have a core 2p orbital and so does not rise rapidly with pressure. The Si 3p rises, but will not be destabilized relative to the ISQ until high pressures, above 500 GPa; its IP is too large to begin with. We predict that

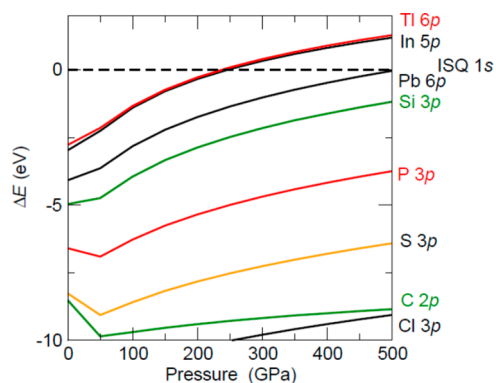


Figure 6. Energies of the frontier orbitals of selected Group 13–17 elements relative to the ISQ in a He-containment model.

Tl and In will form ISQs, and, at higher pressure, Pb also. We plan to explore these predictions in the future.

We have also examined the transition series, Groups 3–10, and selected Group 11 and 12 atoms. The general effect (already noted for Ca) is that the valence d electrons are not very sensitive to pressure, and in the pressure range never rise above the ISQ line. Only Cu has a chance of forming an ISQ, and that only above 500 GPa. The other group 11 and 12 elements have too high IPs to readily form ISQs.

Still another interesting feature of the pressure dependence of orbital energies is an anticipated energy crossing between 2s and 2p orbitals in Li and Be (see Figure S3 in the SI). Because of the lack of inner shell p electrons, the 2p orbital is less sensitive to the pressure than the 2s orbital; the latter has to stay orthogonal to the inner shell 1s orbital. As a result, the 2s energy may become higher than that of 2p under increasing pressure (the electron in a spherical container model predicts just that, as we will soon see). As shown in the SI, this happens around 100 GPa for Li, but does not happen for Be below 500 GPa. This 2s/2p level inversion under pressure in Li has also been noted earlier.^{16,42}

In our considerations, an essential role is played by the presence or absence of cores of the same angular momentum, by ionization potentials, and, crucially, by the relative slopes of different angular momentum quantum number (l) frontier orbitals of compressed atoms with pressure. That the energy of d levels varies least with pressure, p levels next, and s levels most is not new to us. Following a suggestion by Fermi, Sternheimer probably was the first to calculate this pattern (for s and d, in the context of the s–d transition in Cs),⁴³ followed by others.⁴⁴ Let us see why the regularities we and others have calculated make sense.

■ THE REASON FOR THE VARIATION OF ENERGIES OF CONFINED ATOMS, AND SOME RULES FOR FORMING ISQs

In the blow-by-blow analysis of various elements across the Periodic Table, we have seen a determining feature, a great variation in the slope of the energies of various types of frontier orbitals as a function of pressure. Outer s levels increase most with increasing pressure, p levels least, and d levels are essentially flat (all relative to the ISQ) in the pressure regime studied; they will rise at higher pressures.

Why this distinctive differentiation of the slopes of levels with pressure? Another time-honored spherical containment model, that of a screened Coulombic potential in a bounding surface,

provides understanding here. Actually, a family of such potentials may be described as follows, where R is the distance of an electron from the center of the sphere that contains it: (1) $V = \text{const} = -Z_{\text{eff}}/R_1$, for $R \leq R_1$; (2) $V = -Z_{\text{eff}}/R$ for $R_1 \leq R \leq R_2$; (3) $V = +\infty$, for $R = R_2$. For $Z_{\text{eff}} = 1$, $R_1 \rightarrow 0$, $R_2 \rightarrow \infty$ this is the hydrogen atom; for $R_1 = 0$, R_2 finite, a compressed hydrogen atom; for $R_1 \rightarrow R_2$, both large, we approach the particle in a potential-less spherical container with infinite walls. In between, we have a particle in a spherical container with a variously sculpted potential energy floor, a playground well-explored in modeling core potentials.

The problem has attracted a multitude of theorists.⁴⁵ All the bound states of this potential rise in energy with diminishing R_2 (whose inverse cube is a rough surrogate for pressure increasing), or with increasing R_1 ; some part of the attractive Coulomb potential is cut off, one way or another. More importantly for our story is that the boundary conditions, working through the radial quantization, have a profound effect on the degeneracies. That 2p goes below 2s, and 3d below 3p below 3s at the radius of the sphere decreases, for an unscreened Coulomb potential, is well-established in the perturbation theory studies cited. Actually, a theorem can be proved that the quantum mechanical Runge–Lenz-vector-conservation-caused degeneracy of the Coulomb potential is broken, and, moreover, for any n and l , $E(n, l+1) < E(n, l)$.⁴⁶

A simple physical way of seeing what happens is to think about, say, the effect of pressure on 3s, 3p, 3d orbitals. A plot of the radial electron density distribution for a hydrogen atom shows that the density goes as $3s > 3p > 3d$ at large radius. So the constraint of pressure, always destabilizing, will affect a 3s orbital more than a 3p, and that in turn more than a 3d. To put it another way, 3s has two radial nodes, 3p one radial node, and 3d none. As the space far from the nucleus is cut off by a bounding surface that serves to model the application of pressure, nodes “hurt” and the natural ordering will be 3d below 3p below 3s.

The effect of applying pressure on an atom is thus to move it from the Coulomb l degeneracy for a given n toward the particle-in-a-spherical-container-with-a-flat-potential-bottom limit of an energy level ordering $1s < 1p < 1d < 2s$. As pressure is applied, the orbitals rise in energy, with the combined effect being that the slope in energy as a function of pressure is less for a level of higher l than for one of lower l .

The ionization potential (IP) of the frontier electrons also has an obvious influence: the less strongly bound the atom's outermost electrons, the easier will it be for them to be detached and enter an ISQ. We can combine the orbital and IP effects into a set of approximate rules of thumb for the formation of ISQs:

Rule of Thumb #1 (Increasing Ionization Potential)

In general, and for elements in the same group in particular, it becomes harder to form an HPE with increasing IP of the frontier electrons. This regularity can be rephrased in terms of the effective (screened) charge on an atom, which sets the IP.

Rule of Thumb #2 (Effect of Incompressible Core)

ISQ formation is more likely when the valence electrons, s or p, move around a relatively incompressible core. For example, it is easier for Al and Mg to form HPEs than B and Be. This is also why Li and Na form HPEs readily.

Rule of Thumb #3 (Effect of d Orbitals)

Energies of d orbitals do not increase significantly with pressure (relative to s and p orbitals, and over the moderate range of pressures we examine, <500 GPa). The primary effect of the low slope with pressure of nd electrons is that the heavier alkali and alkaline metal elements will not readily form ISQs, despite their low IPs; as pressure is applied, their s electrons will transfer to the next available d orbitals. However, the Pickard and Needs result on K^{41} is cautionary; one has to consider the possibility of magnetic electrone phases for the heavier alkali metals.

As a consequence of these regularities, at pressures below or not much higher than 500 GPa, we expect ISQs to form, and HPE behavior for all the alkali metals (with the heavier elements in this group being a special case), Al, and, near the high end of this pressure range, for Mg, Si, Tl, In, and Pb.

POSSIBILITIES

In a forthcoming paper, we analyze in detail the electronic structure of two high pressure electrides, Na and Mg, and look at some others in the terapascal regime. We see there that ISQs in high pressure electrides sometimes occupy volumes that are very much like real inorganic anions, converting a metallic crystal at low pressure into an ionic solid, mimicking a binary compound, at elevated pressures. We are hardly the first ones to notice this.^{13,15,19,23,26,41,47} We also see, as in the case of the HPE of Mg,²⁵ and in several $P = 1$ atm electrides,⁶ that at times the electrone regions overlap, and if the electron counts allow it, one gets a metal. Magnetic electrides have been suggested, and there are other possibilities, which we will explore, of “molecular” ISQs.

SUMMARY

We build a predictive model of high pressure electrides, one which also explains which elements will form HPEs at moderately elevated pressures. And which will not. A region of interstitial space, which we call an interstitial quasi-atom (ISQ), will have well-quantized levels. On compression, the energy of any electrons in the orbitals of an ISQ increases, but less so than the energy of the outermost electrons of similarly compressed atoms. Therefore, at a certain pressure, the transfer of the electrons from atomic orbitals to the orbitals of an ISQ is enthalpically favored.

To gain more specificity, we explore a semiquantitative model in which interstitial space and atoms are confined in a compressed He lattice. The governing regularities are set by the very distinct slopes of the atomic energy levels with pressure. To explain these, we use a simple model for the ISQ that fits the He-confinement calculations pretty well: an electron bound in a flat-bottom spherical potential with steep walls. And for the atoms, a Coulomb pseudopotential with steep spherical wall confinement as well.

The effect of impinging walls on a Coulomb potential, with its limit of an atom in a spherical container, has a critical (and, in the context of HPEs, a controlling) physical consequence: the slope in energy with increasing pressure of different angular momentum quantum number orbitals/electrons differs essentially. d orbitals go up gently in energy (as the pressure increases), p orbitals more steeply, and s orbitals most steeply. Whether an orbital of a given l has a core orbital of the same l below it in energy is critical.

Three rules of thumb for the formation of HPEs follow from both these theoretical considerations and form a direct model in which a He lattice is used as compression medium: (1) It becomes harder to form a HPE with increasing IP of the frontier electrons. (2) ISQ formation is more likely when the valence electrons, s or p, move around a relatively incompressible core. (3) It will be very hard to form HPEs of elements with valence d electrons.

Our direct model predicts that across the Periodic Table, below ~ 500 GPa, HPEs are likely to form for Li, Na, Al, and, near the high end of this pressure range, for Mg, Si, Tl, In, and Pb. Magnetically coupled electrides are also a possibility for the heavier alkali metals.

■ ASSOCIATED CONTENT

Supporting Information

Further references on $P = 1$ atm electrides; An attempt to define an electride; Further details of the helium confinement model; A potential s/p crossing under pressure; Energy levels of a particle in a spherical box, and comments on a confined spherical harmonic oscillator. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Mao-Sheng Miao is a visiting professor in Beijing Computational Science Research Center and an associate specialist at the University of California Santa Barbara. He works in overlapping areas in chemistry, physics, and materials science, using first principles computation methods.

Ronald Hoffmann is the Frank H. T. Rhodes Professor of Humane Letters Emeritus at Cornell University, where he has been from... before you were born. The pedagogical imperative is strong in his work; his research papers are written for the graduate student, sometimes to the consternation of editors and reviewers. He has worked theoretically on all parts of chemistry except the biochemical, and has built his own land between chemistry, philosophy, and poetry.

■ ACKNOWLEDGMENTS

We are grateful to Neil Ashcroft, Greg Ezra, Huayun Geng, Paul Loubeyre, and Xiao-qiu Ye for discussions, information, and computational assistance. M.-S.M. is supported by the MRSEC program (NSF-DMR1121053) and the ConvEnergERT Program (NSF-DGE 0801627). The calculations made use of CNSI computing clusters (CNS-0960316) and NSF-funded XSEDE resources (TG-DMR130005). The work at Cornell was supported by Efree (an Energy Frontier Research Center funded by the Department of Energy (Award Number DESC0001057 at Cornell, subcontract to Carnegie Institution of Washington)).

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