High Pressure Electrides: A Predictive Chemical and Physical Theory

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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 J. Dye on ambient pressure electrides. Nor the 200-year-old history of metal-ammonia solutions. Nor the remarkable alkali metal suboxides, as well as other ambient condition electrides. 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, Li, and Cs. Experimental observations and theoretical calculations for Li and Na 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. The first explicit suggestion that the unusual high pressure phases are to be viewed as electrides is due to Y. Ma and coworkers; the idea is clearly there also in the work of E. G. Maksimov, M. G. Magnitskaya, and V. E. Fortov.

Computational work points to possible HPE formation in elements beyond the alkali metals: in Al at 5 terapascals (TPa), Mg at 800 GPa, and C at 25 TPa. The HPE phenomena is observed or predicted in compounds as well as elements. These are as diverse as MgO2, 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 Ashcroft 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...
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 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 × 3 × 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 × 3 × 3 FCC supercell minus one He), we maintain the point group symmetry (O<sub<h></sub>). 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 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

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.
The wave functions of this familiar problem
e(s) are spherical Bessel functions, and the energy levels can be expressed as

\[ E(n, l) = \frac{z_{nl}}{2mR_s^2} \frac{h^2}{2mR_s^2} \]

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 \( z_{nl} \) 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 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 \( R = D_0 - R_e \) for the orange line, the radius reduction \( R_e \) is taken as the half of the He–He distance in FCC.

The red line is the best fit to the actual ISQ calculations, \( R_e = 0.3 \) Å.

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, \( R = D_0 - R_e \). For the orange line, the radius reduction \( R_e \) is taken as the half of the He–He distance in FCC. The red line is the best fit to the actual ISQ calculations, \( R_e = 0.3 \) Å.

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 electrode formation 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 electrode formation through electron density and electron localization function (ELF) plots. Both theory and experiment point to electrode formation in Li and Na in the 50–80 GPa range, where our simple model predicts it. There is as yet no evidence for Mg and Al electrides at moderate pressure, 250–400 GPa. But at higher pressure, electrode behavior was predicted for Al\(^{12}\) 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 electrons 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.\(^\text{41}\) 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 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 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 K\(^\text{38}\) and Ca\(^\text{23}\) as well as for other alkali metals.\(^\text{39}\) Electride formation as well as d-orbital occupation, has been predicted for Ca at moderate pressures.\(^\text{10,23,40}\) 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.\(^\text{41}\) In the case of K, the prediction is that a ferromagnetic electrode 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 Ti 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.\(^\text{16,42}\)

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),\(^\text{43}\) followed by others.\(^\text{44}\) 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 next, 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 $Z_{\text{eff}} = 1$, $R_1 \to 0$, $R_2 \to \infty$ this is the hydrogen atom; for $R_1 = 0$, $R_2$ finite, a compressed hydrogen atom; for $R_1 \to R_2$, 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. 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 $3p$ on the degeneracies. That $2p$ goes below $2s$, and $3d$ below $3p$ on the degeneracies. For $Z_{\text{eff}} = 1$, $R_1 \to 0$, $R_2 \to \infty$ this is the hydrogen atom; for $R_1 = 0$, $R_2$ finite, a compressed hydrogen atom; for $R_1 \to R_2$, both large, we approach the particle in a potential-less spherical container with infinite walls.

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 $K^{31}$ is cautionary; one has to consider the possibility of magnetic electrode 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, Ti, 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. We also see, as in the case of the HPE of Mg, and in several $P = 1$ atm electrides, that at times the electrode 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 \( \sim 500 \) GPa, HPEs are likely to form for Li, Na, Al, and, near the high end of this pressure range, for Mg, Si, Ti, 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 electrode; 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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The authors declare no competing financial interest.

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### References


(30) This value was checked against the experimental equation of state of dense helium, obtained from Paul Loubeyre, private communication.

(31) The VASP program adds a uniformly distributed positive charge to compensate for the charged unit cell in the model.


(37) There is more to the Al story, as the SI describes.


