

# High Pressure Electrides: A Chemical and Physical Theory

*Mao-sheng Miao and Roald Hoffmann*

Beijing Computational Science Research Center, Beijing 10084, P. R. China and Department of Physics,  
California State University Northridge, CA  
Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY

**Accts. Chem. Res. 2014, 47, 1311–1317**  
**J. Amer. Chem. Soc. 2015, 137, 3631-3637**  
**Angew. Chem. Int. Ed. 2017, 56, 972-075**



M.S.M. is supported by the MRSEC program (NSF-DMR1121053) and the ConvEne-IGERT Program (NSF-DGE 0801627). He acknowledges gratefully the NSF-funded XSEDE resources (TG-DMR130005).

# Electrides, at ambient and high pressure

Jim Dye, *Acc. Chem. Res.* **42**, 1564 (2009).

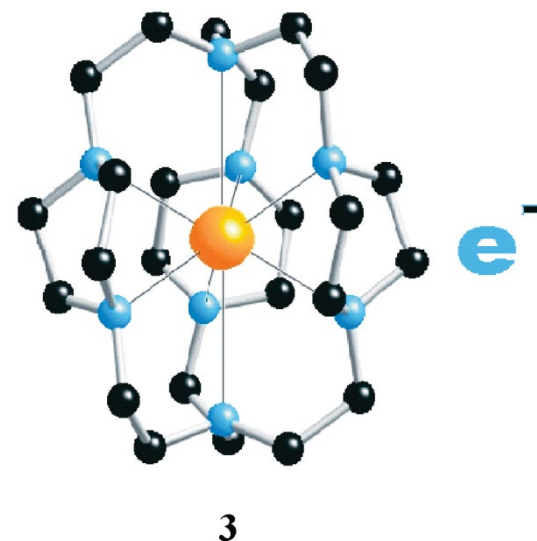
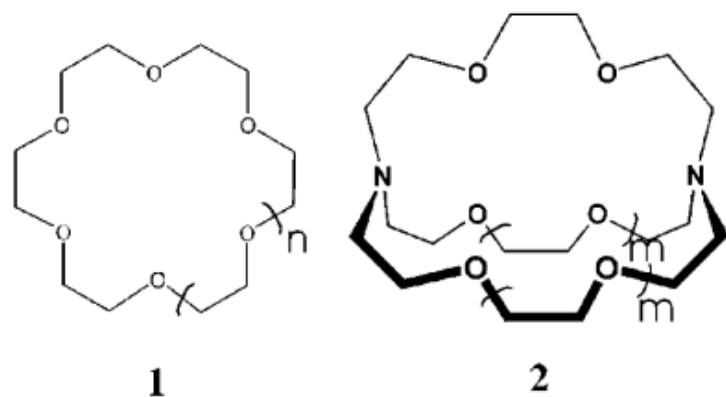


FIGURE 1. Crown ethers and cryptands used to prepare electrides: **1**, ( $n = 0$ ) 15-crown-5 (15C5); ( $n = 1$ ) 18-crown-6 (18C6); **2**, ( $m = 0$ ) cryptand[2.1.1] (C211); ( $m = 1$ ) cryptand[2.2.2] (C222).

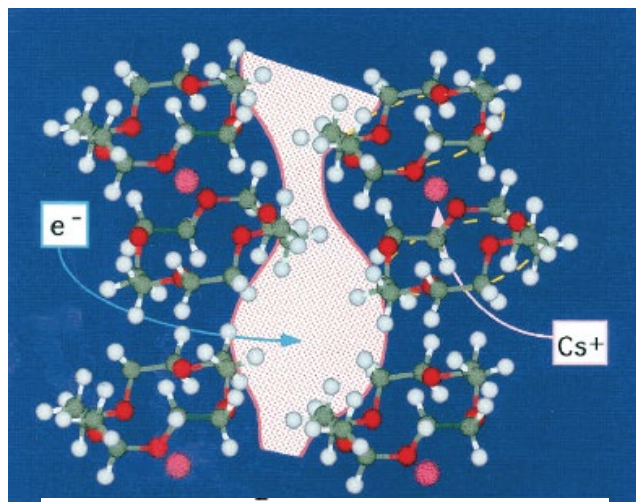
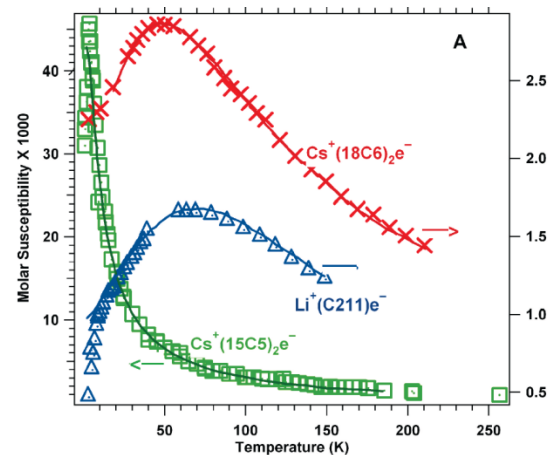
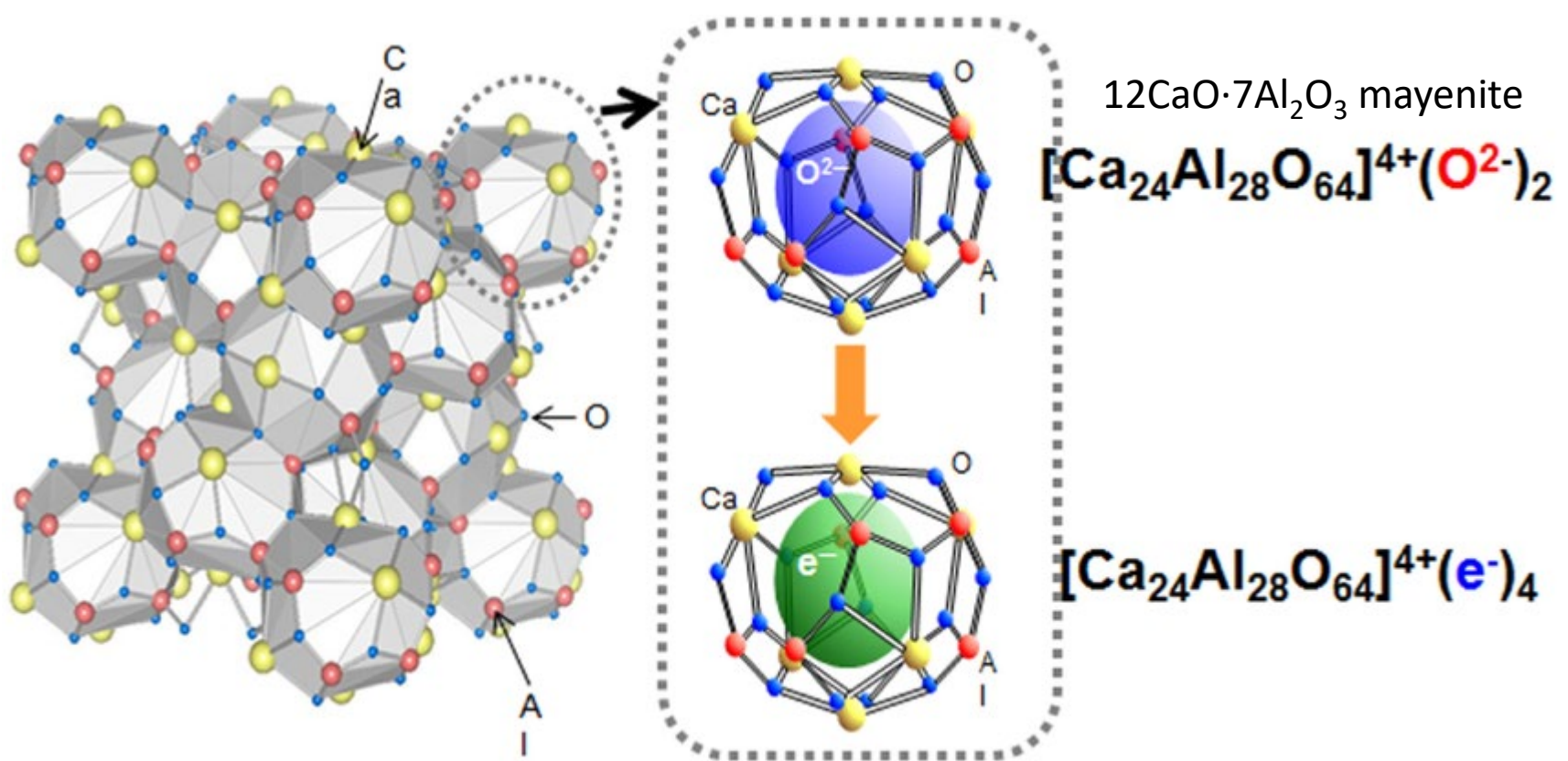


FIGURE 5. The first crystalline organic electride,  $Na^+$ -(tri-pip-aza 222)- $e^-$ , that is stable up to room temperature. Nitrogens are shown in blue, carbons in black, and  $Na^+$  in orange.



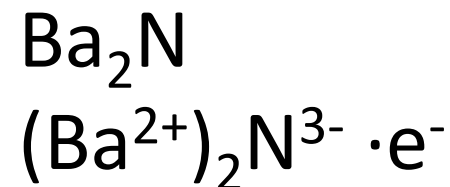
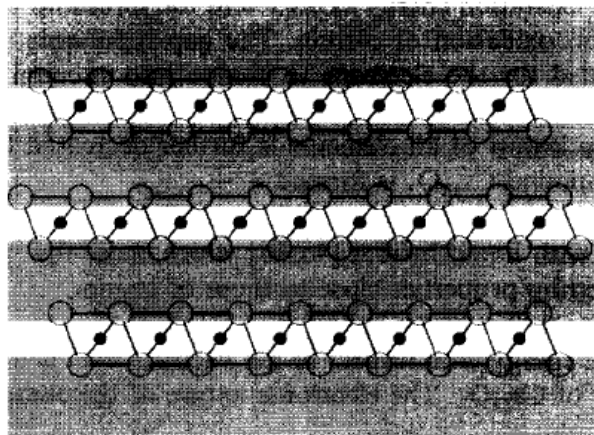


K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano and H. Hosono, Light-induced conversion of an insulating refractory oxide into a persistent electronic conductor, *Nature*, 2002, 419, 462–465. Colorless solid to black metal, work function 2.4 eV.

# Metallic Electrides

at 1atm

Arndt Simon, Group 1 and 2 Suboxides and Subnitrides - Metals with Atomic Size Holes and Tunnels. *Coordination Chemistry Reviews* **1997**, 163, 253-270.



Lee, K.; Kim, S. W.; Toda, Y.; Matsuishi, S.; Hosono, H. Dicalcium Nitride As a Two-Dimensional Electride with an Anionic Electron Layer. *Nature* **2013**, 494, 336-340.

(a)

Nov.

When 8 grains of potassium were heated in ammoniacal gas - it assumed a beautiful metallic appearance & gradually became of a fine blue colour

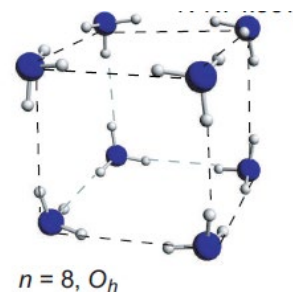
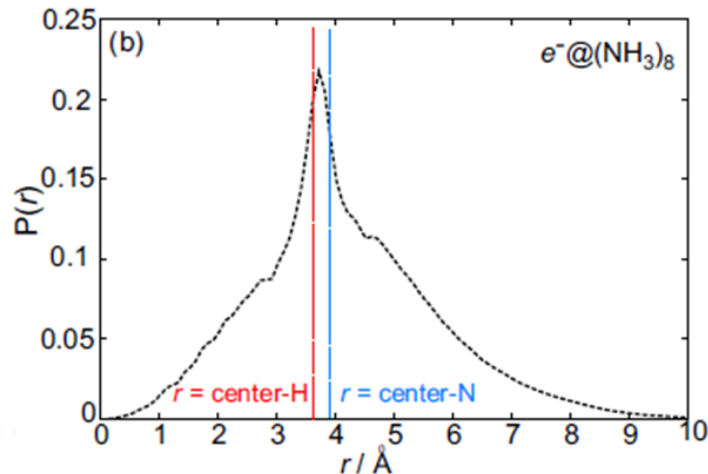
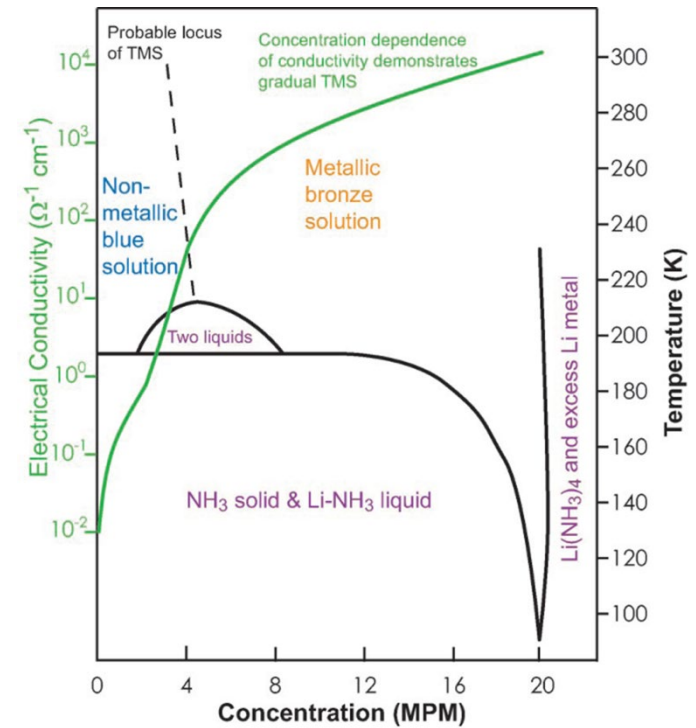
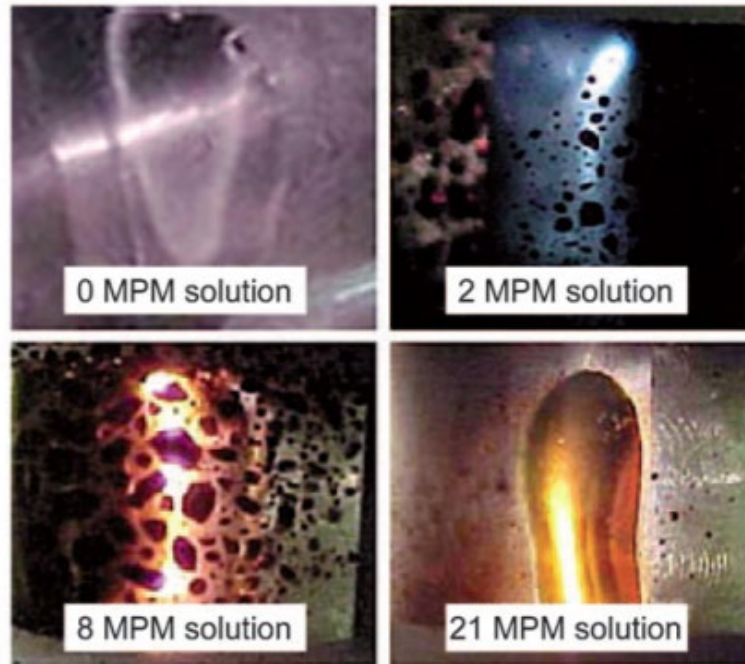
(b)

Nov 15<sup>th</sup>

Twelve cubic inches of ammonia were made to act on nine grains of potassium in a green glass retort exposed to the heat of a spirit-lamp, an ebullition of the potassium took place, & its fine silver-color, became blue, which was soon changed to a green, it then soon its original color but not its splendor.

Two entries from the laboratory notebook of Sir Humphry Davy for the period October 1805–October 1812. a) 14 November 1808: “When 8 grains of potassium were heated in ammoniacal gas—it assumed a beautiful metallic appearance and gradually became a fine blue colour.” b) 15 November 1808: “Twelve cubic inches of ammonia were made to act on nine grains of potassium in a green glass retort exposed to the heat of a spirit-lamp, an ebullition of the potassium took place, and its fine silver-color became blue, which was soon changed to green, it then recovered its original color but not its splendor.”

# Alkali metal ammonia solutions

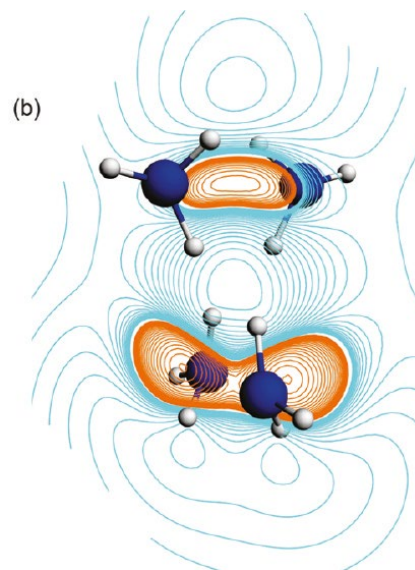
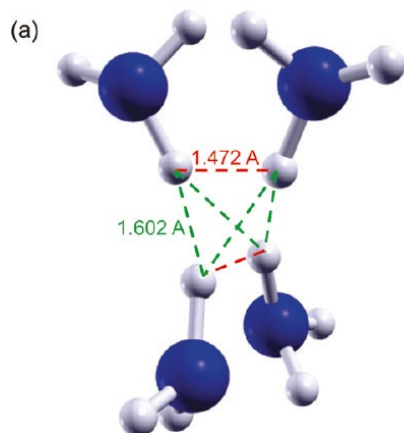
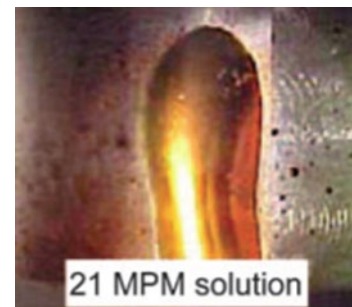


Mike Sienko

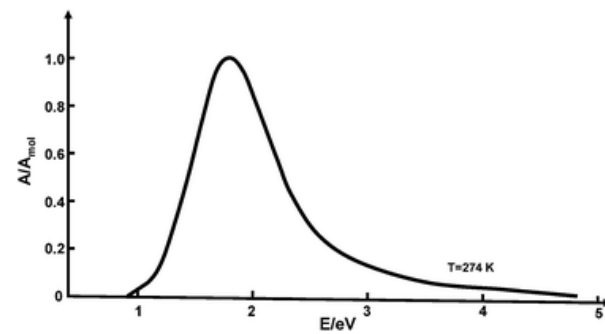
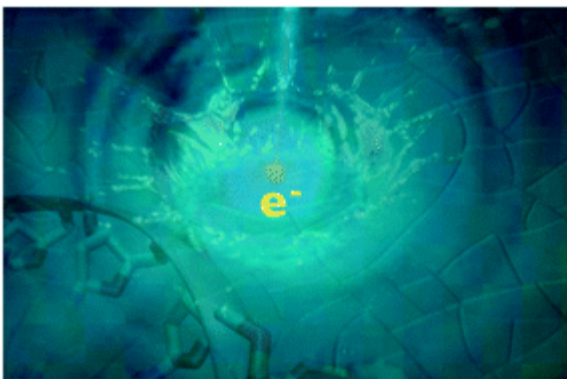
A Molecular Perspective on Lithium-Ammonia Solutions, *E. Zurek, P. P. Edwards, and R. Hoffmann, Angewandte Chem. Int. Ed. Engl., 48, 8198-8232 (2009)*

**(Barely) Solid  $\text{Li}(\text{NH}_3)_4$ : The Electronics of an Expanded Metal.** E. Zurek, X.-D. Wen, and R. Hoffmann. *J. Am. Chem. Soc.* 133, 3535-3547 (2011).

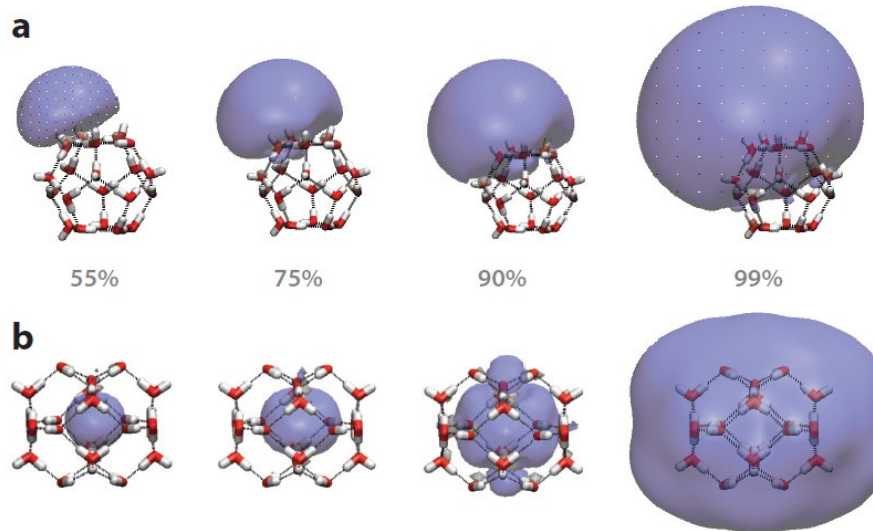
Lowest melting solid (90K) by >100 degrees  
[https://youtu.be/Mv\\_enhLlea8](https://youtu.be/Mv_enhLlea8)



# The Hydrated Electron

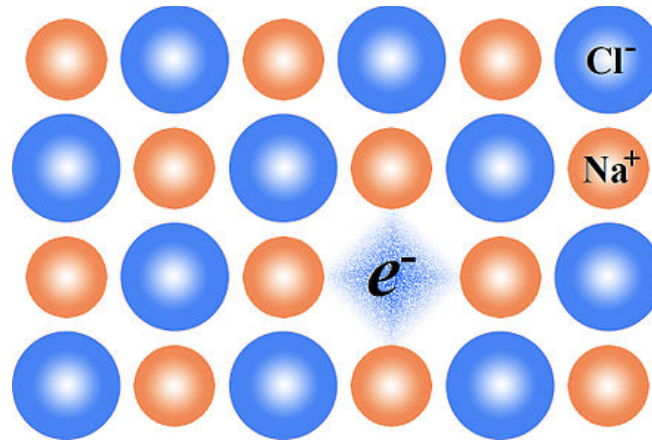


J. M. Herbert and M. P. Coons, *Annu. Rev. Phys. Chem.*, 2017, 68, 447-472





## F Centers



Defects in diamond and other structures

General electrone problem



The electrons have a choice:

1. Go into antibonding MOs of A or AB frameworks. This will show up in weakened bonds.
2. Go into Rydberg orbitals (higher principal quantum number orbitals) of A or AB. For, Li 3s or 3p...
3. Reduce (make neutral) some of the cations, leading to formation of regions of metallic A, interspersed with regions of ionic bonding.
4. Stay in space between nuclei.

The choice is not obvious

# high pressure electrifies

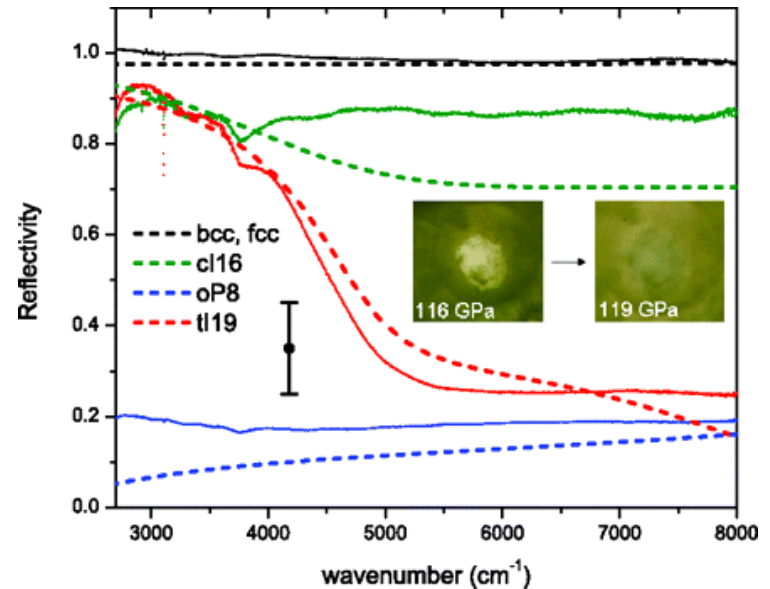
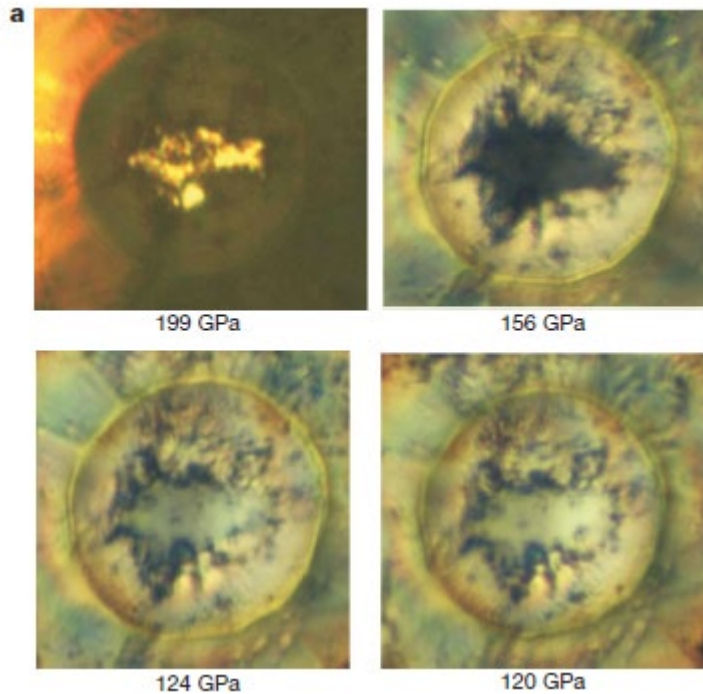
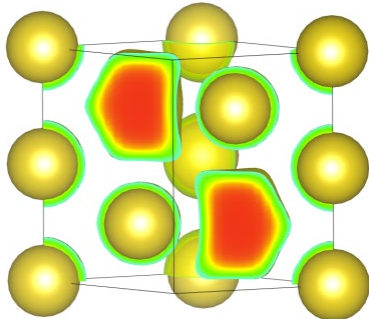


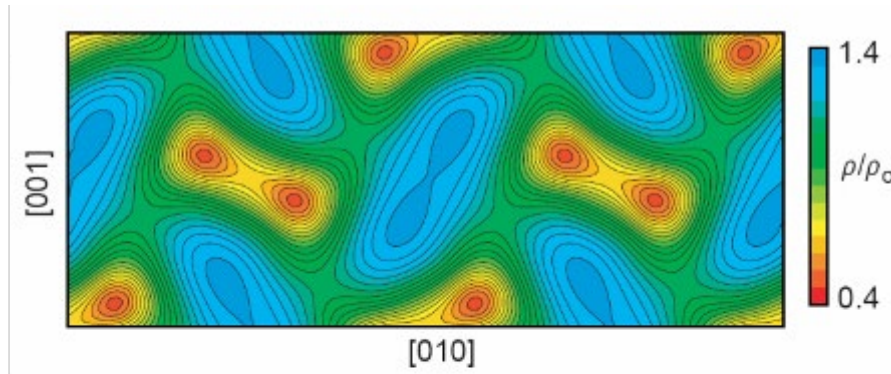
Fig. 1. Reflectivity in the known ambient-temperature phases of Na (bcc and fcc are essentially identical) from experiments (solid lines) and our first-principles density functional theory computations (dashed lines). Experimental data shown are representative spectra. Average error in experimental data (as a result of difficulties in modeling diamond absorption and other effects such as surface inhomogeneities on the sample and references) is shown with the error bar. Broad features, however, are consistent in all experiments. An image of a sample across the cl16  $\rightarrow$  oP8 transition is shown (pressure measured from ruby fluorescence).

Ma, Y.; Eremets, M.; Oganov, A. R.; Xie, Y.; Trojan, I.; Medvedev, S.; Lyakhov, A. O.; Valle, M.;

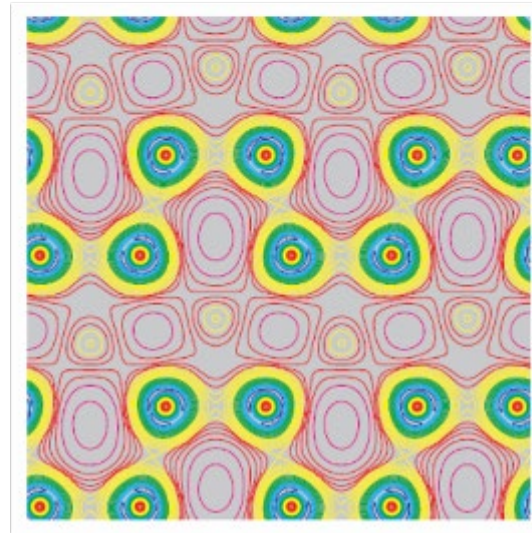
Prakapenka, V. **Transparent Dense Sodium.** *Nature* 2009, 458, 182–U183.



Lazicki, A.; Goncharov, A. F.; Struzhkin, V. V.; Cohen, R. E.; Liu, Z.; Gregoryanz, E.; Guillaume, C.; Mao, H. K.; Hemley, R. J. Anomalous Optical and Electronic Properties of Dense Sodium. *Proc. Nat. Acad. Sci. U.S.A.* **2009**, 106, 6525–6528



## Elemental Li



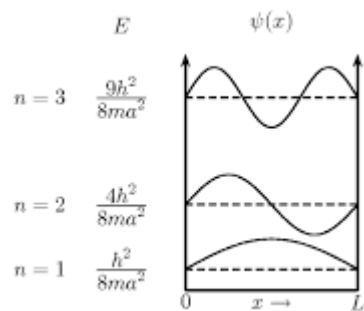
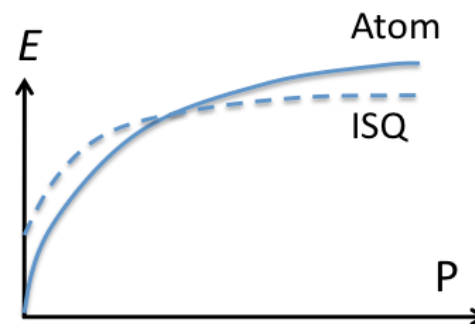
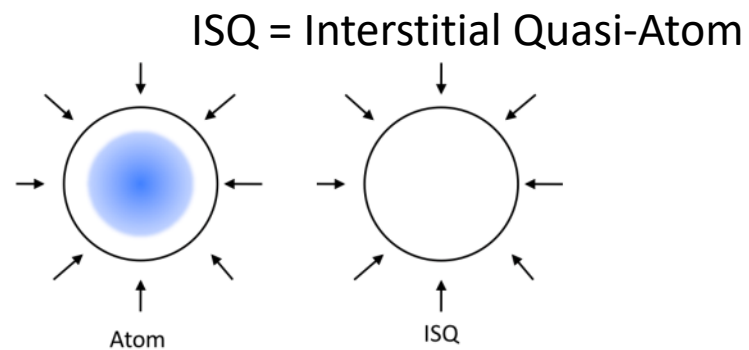
**top:** Neaton, J. B.; Ashcroft, N. W. Pairing in Dense Lithium. *Nature* 1999, 400, 141-144.

**bottom:** Nelmès group 2003

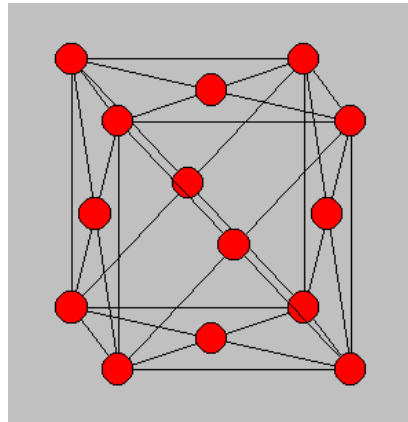
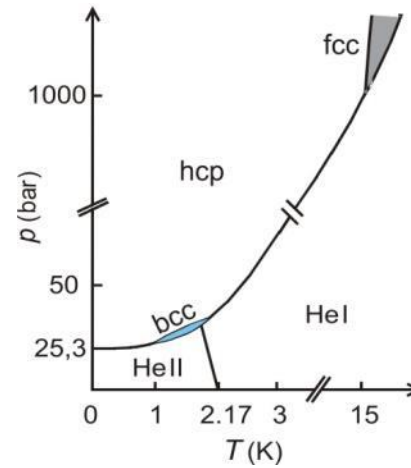
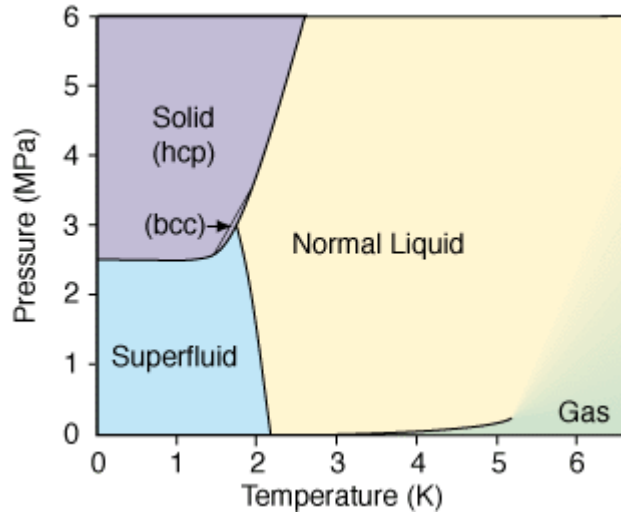
# High Pressure Electrdes: A Chemical and Physical Theory

*Mao-sheng Miao and Roald Hoffmann*

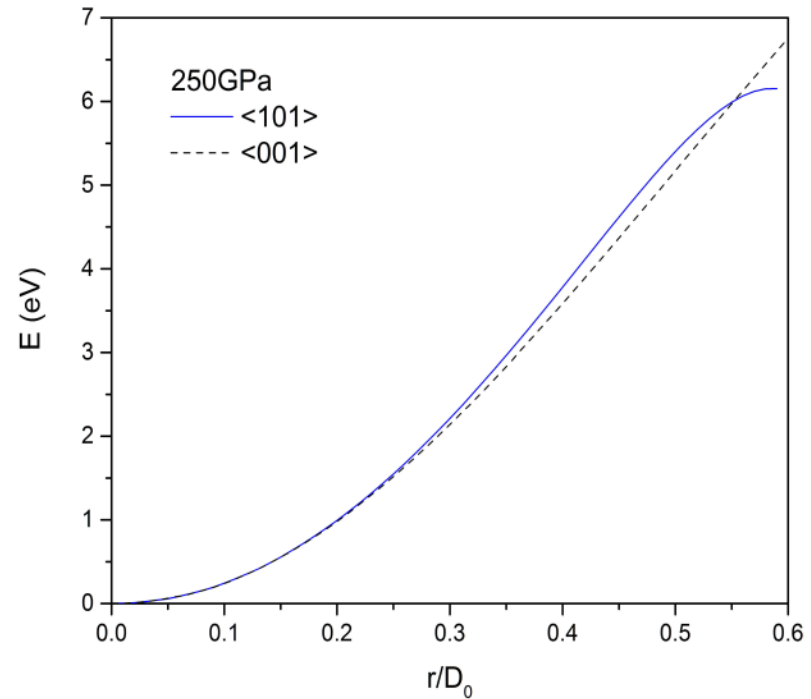
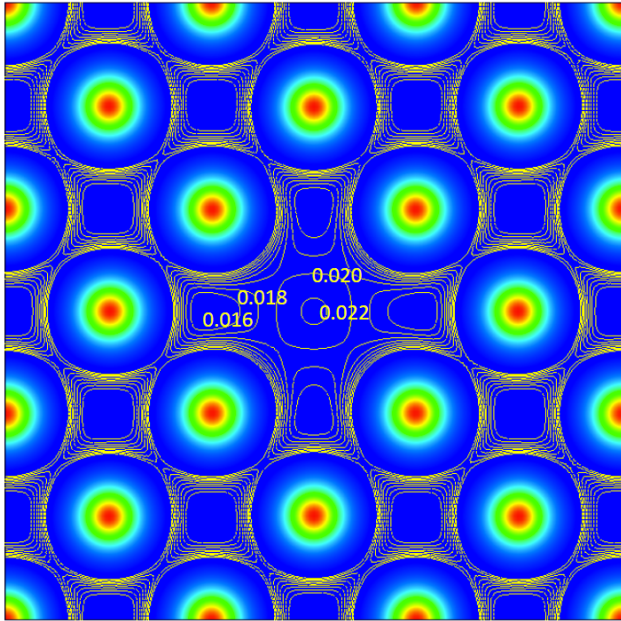
Accts. Chem. Res. 2014, 47, 1311–1317



# He compression model



108 atom fcc model = 3 x 3 x3 nonprimitive cell

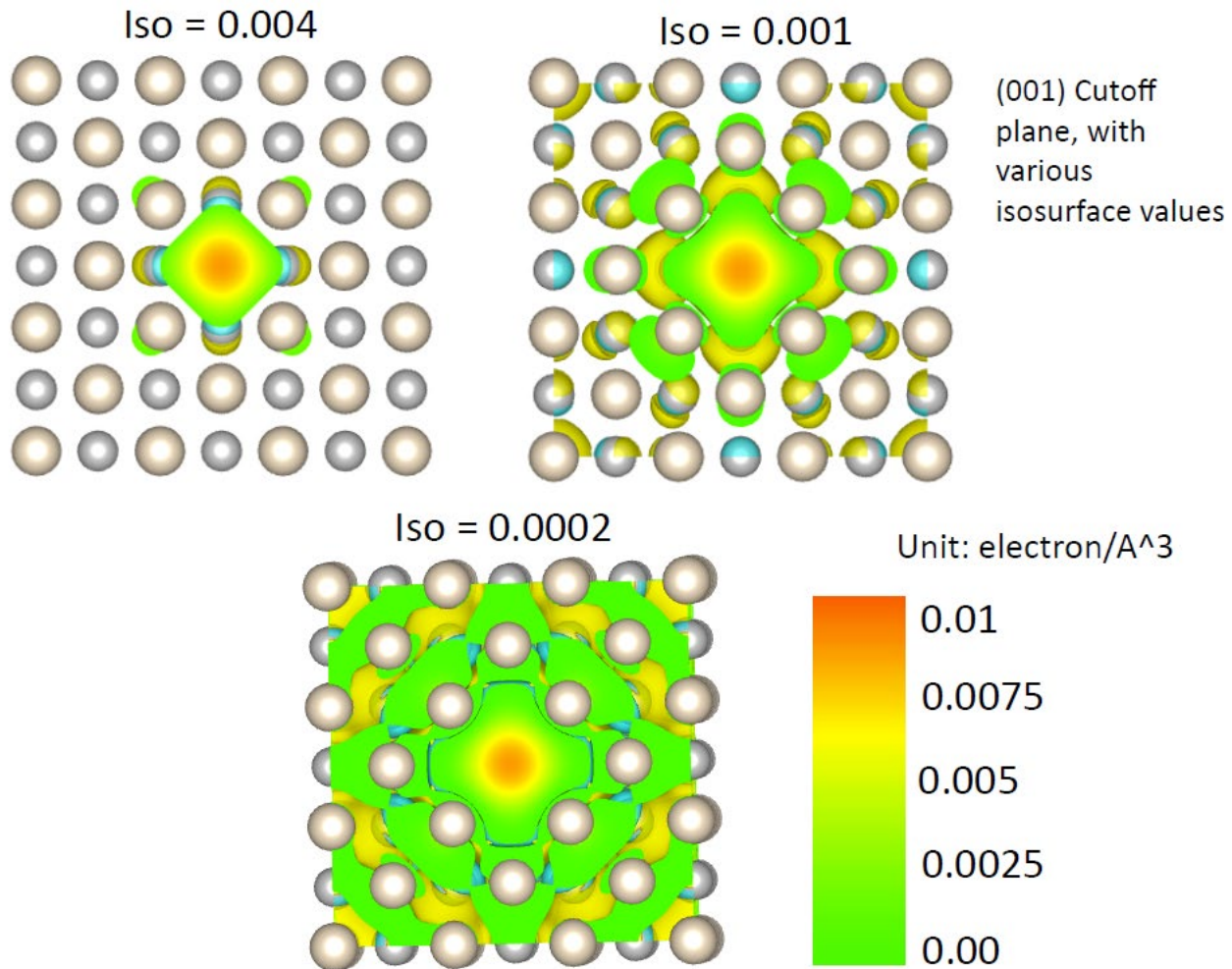


*Potential for electron + He atom comes from* Study of the Properties of an Excess Electron in Liquid Helium. I. The Nature of the Electron—Helium Interactions, Joshua Jortner, Neil R. Kestner, Stuart A. Rice, and Morrel H. Cohen, J. Chem. Phys. 43, 2614-2625 (1965).

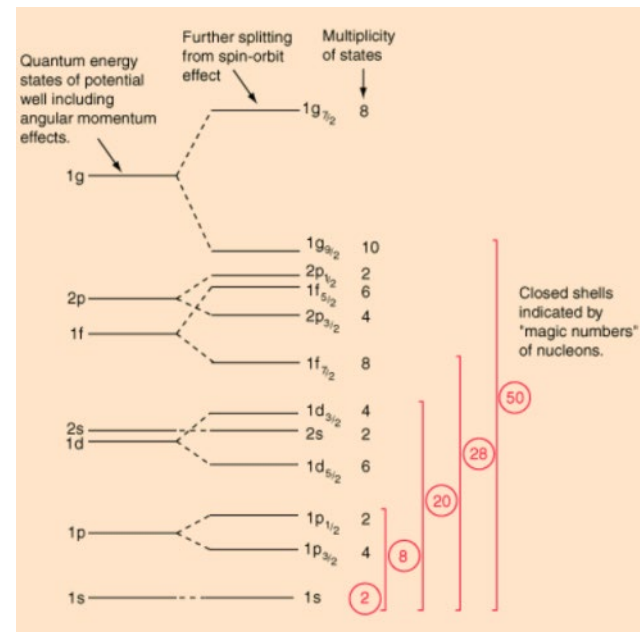
Energy  $E$  of an electron moving along the  $(1,0,1)$  (directly at a surrounding He) and  $(0,0,1)$  (toward the four-fold “hole”) directions of a **cube-octahedron** (He’s located at  $(D_0/\sqrt{2})(\pm 1, \pm 1, 0)$ ,  $(\pm 1, 0, \pm 1)$ ,  $(0, \pm 1, \pm 1)$ ) surrounding the ISQ center. The distance the electron is from the center is given as the dimensionless  $r/D_0$ .  $D_0$  is the optimized distance from the ISQ center to a surrounding He.

Thanks to **Greg Ezra** for help here

# the ISQ 1s level

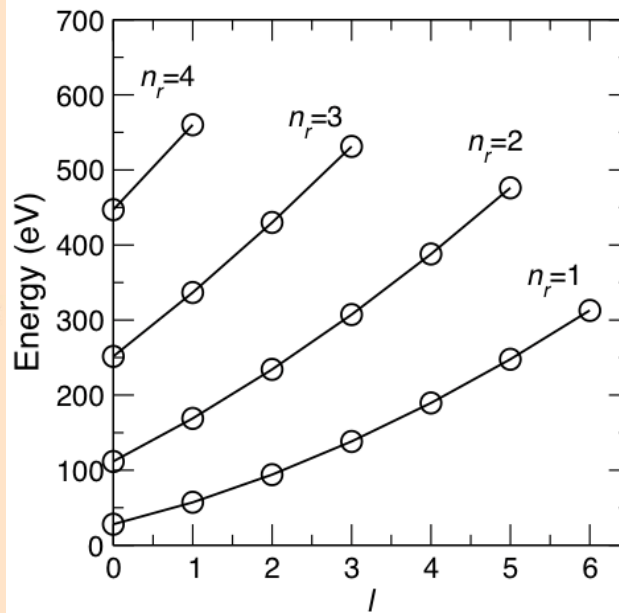






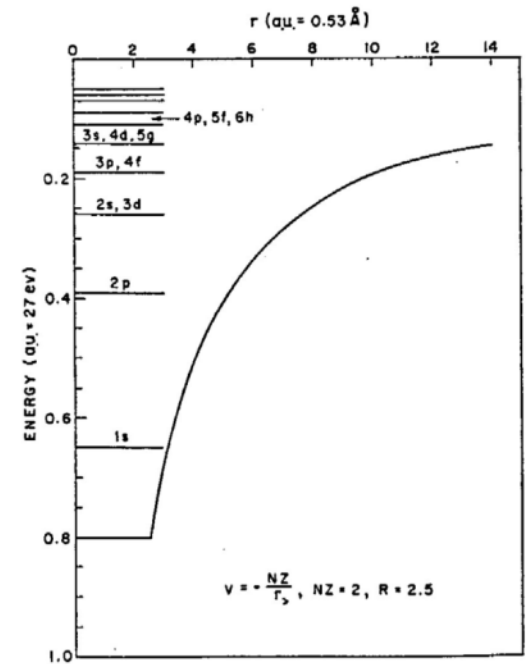
$$E = \left( n_x + n_y + n_z + \frac{3}{2} \right) \hbar\omega$$

3-D harmonic oscillator



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

spherical box

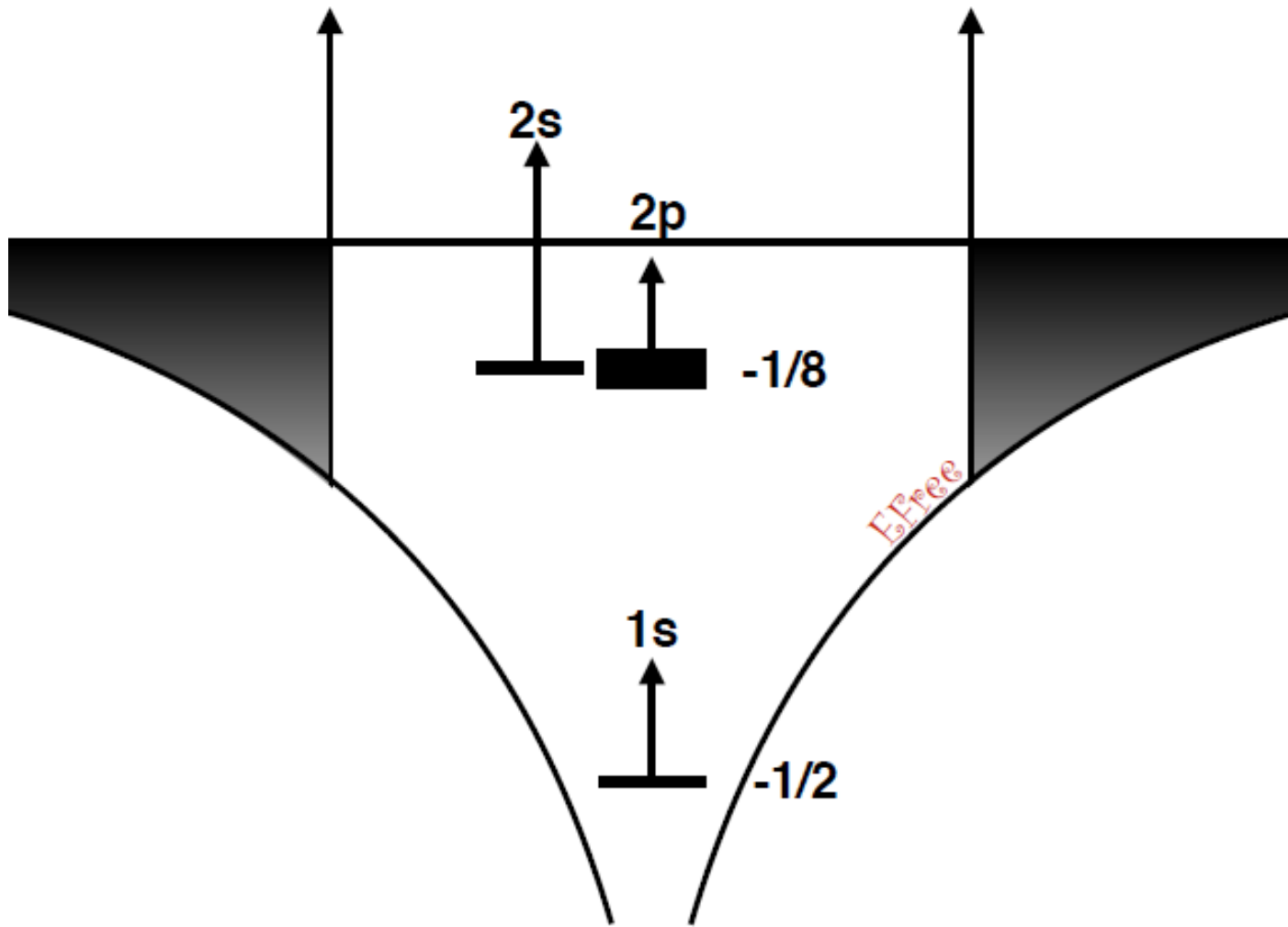


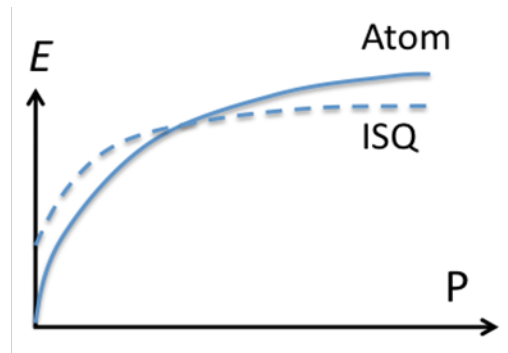
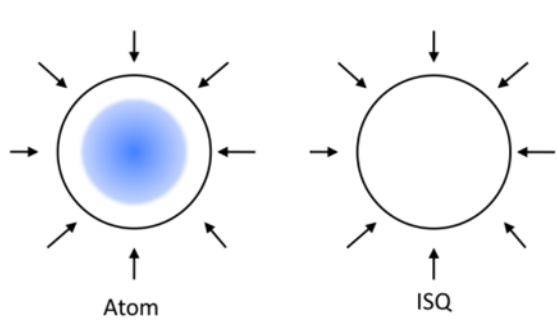
G. H. Wannier, Phys. Rev. 64, 359 (1943).

cut-off Coulomb well

**1s < 1p < 1d ~ 2s**

**Contrast to hydrogenic**  
**1s < 2s=2p < 3s=3p=3d**





ISQ = Interstitial Quasi-Atom

## under pressure, radial nodes hurt...

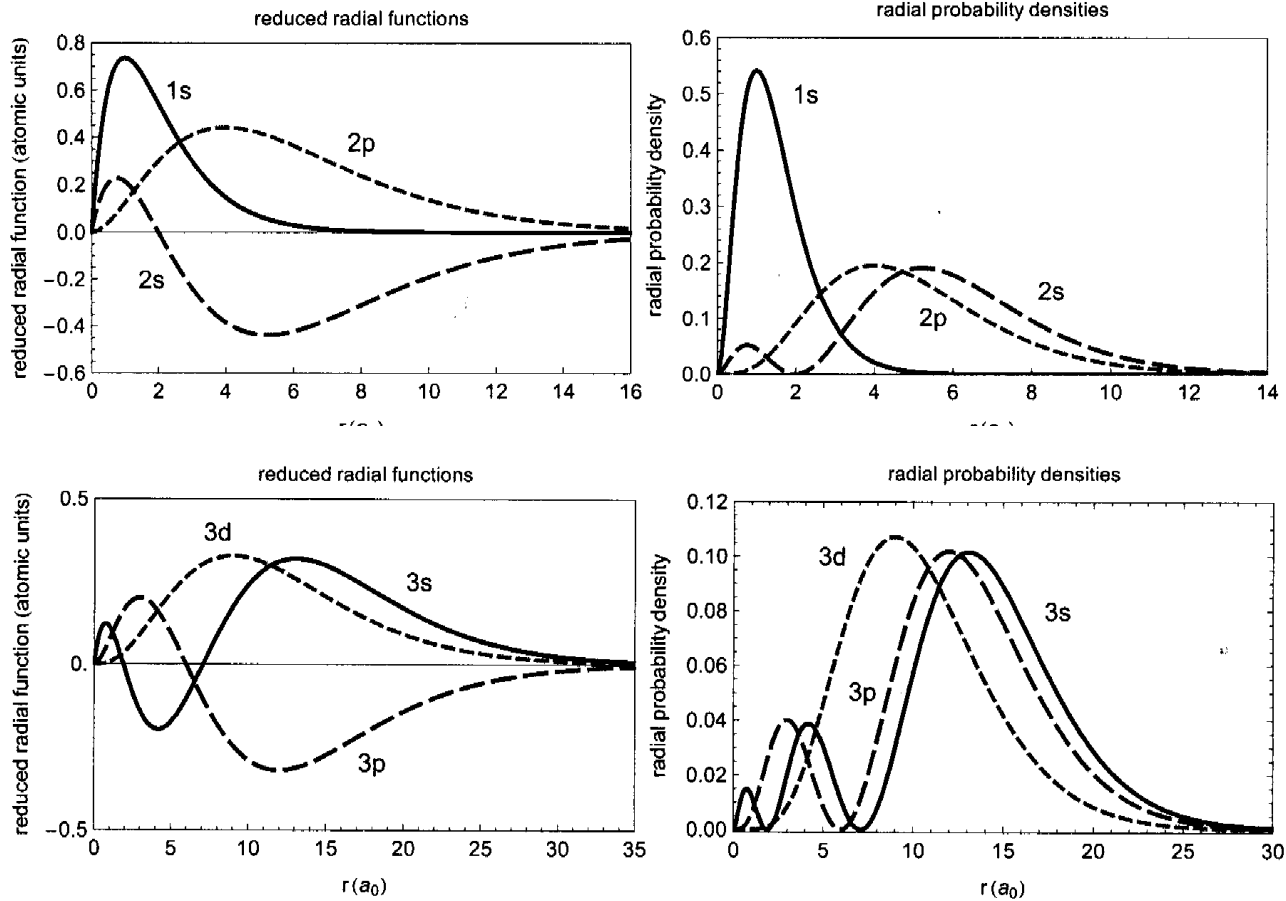


FIGURE 5.3. *Reduced radial functions (upper panel) and radial probability densities (lower panel) for the  $n = 3$  states of atomic hydrogen.*

## under pressure, radial nodes hurt...

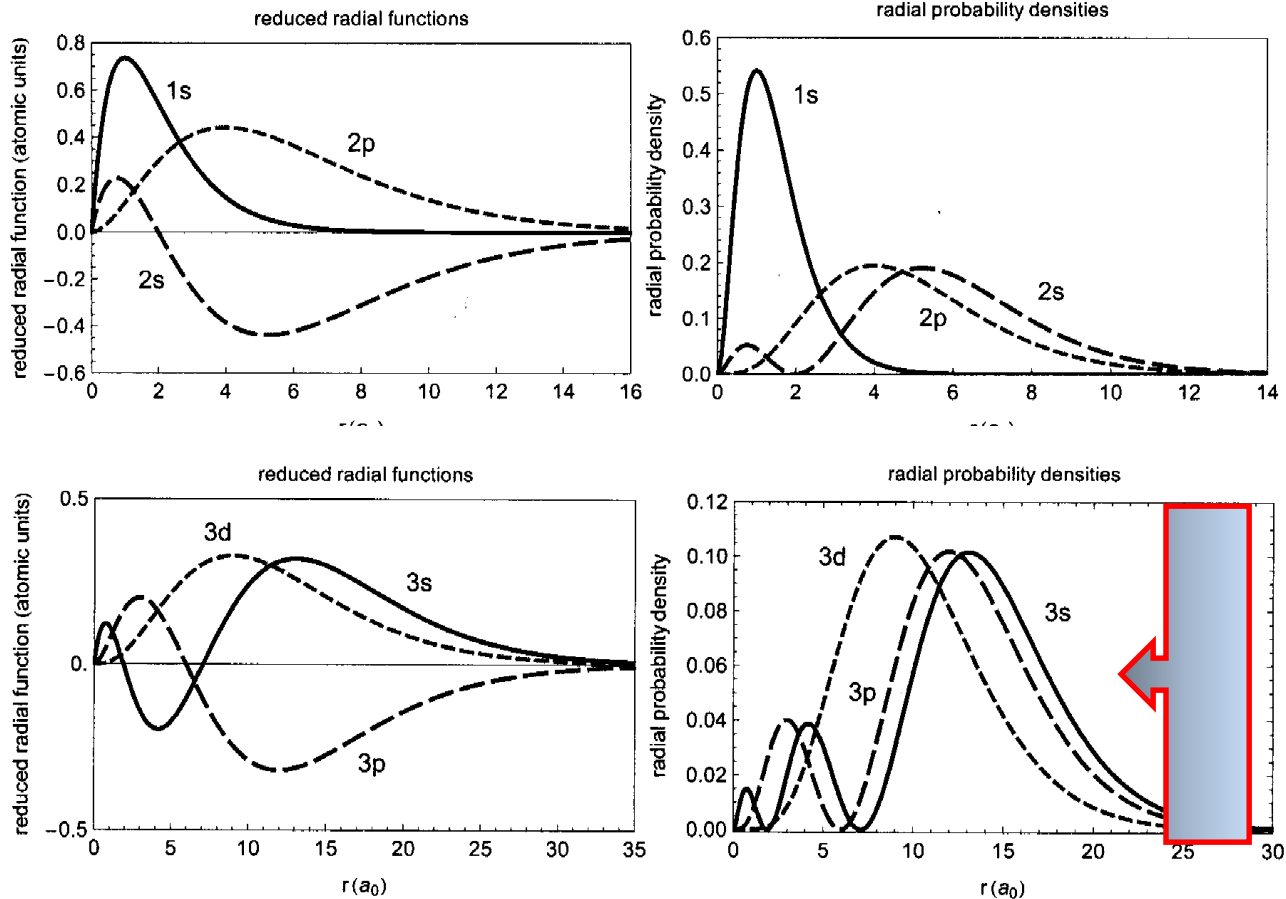
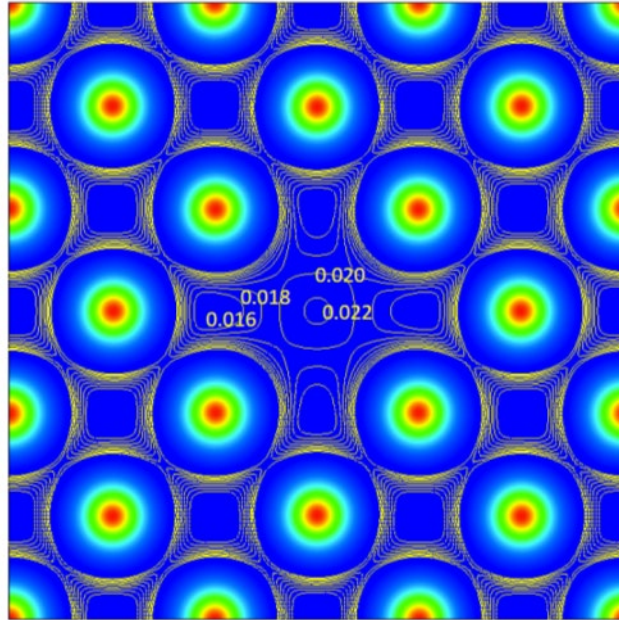


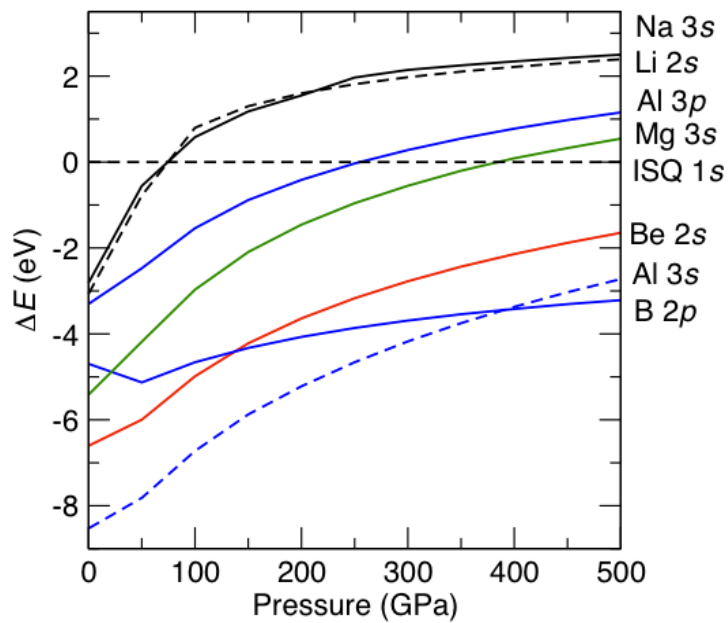
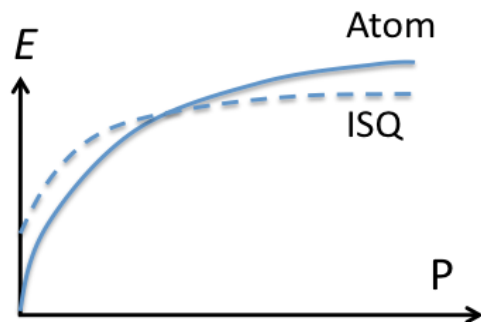
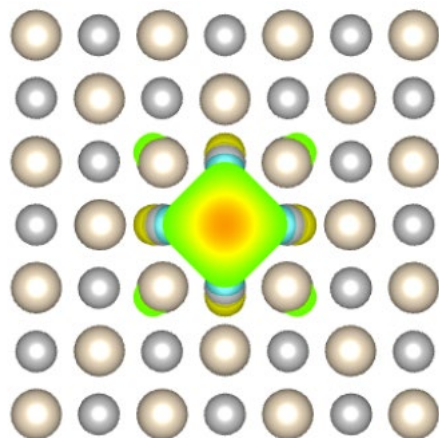
FIGURE 5.3. *Reduced radial functions (upper panel) and radial probability densities (lower panel) for the  $n = 3$  states of atomic hydrogen.*

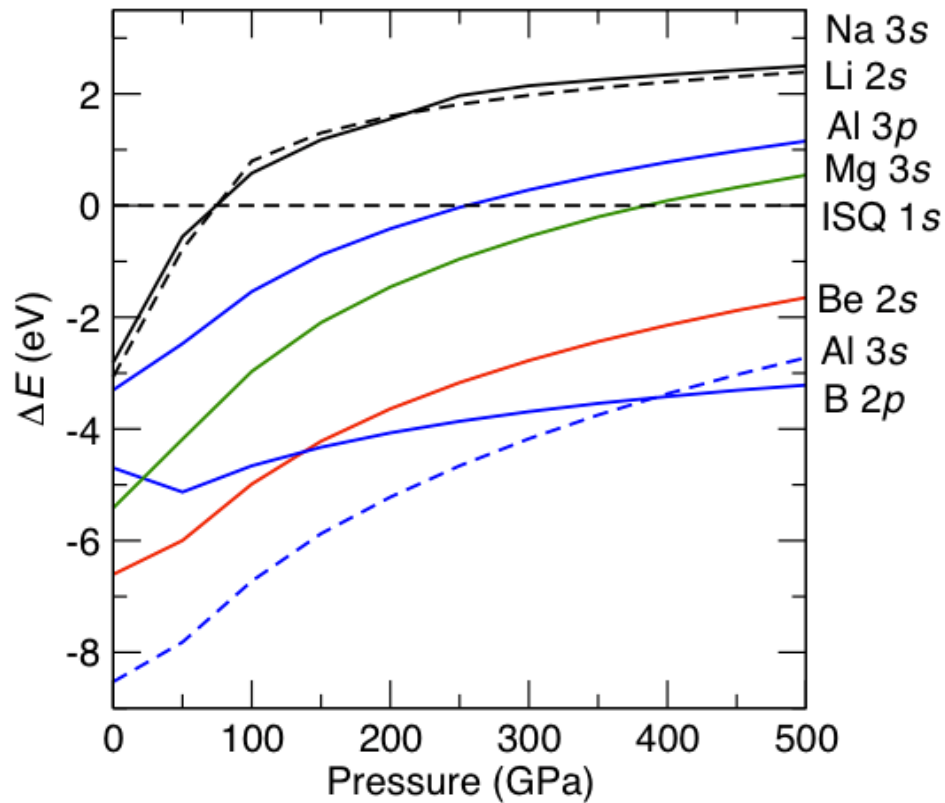
Or... start from a hydrogenic atom  $1s < 2s=2p < 3s=3p=3d$

apply a confining potential, with the result that  $2p < 2s$ ,  $3d < 3p < 3s$

Important: **Effect of pressure greatest on s levels, less on p, least on d**





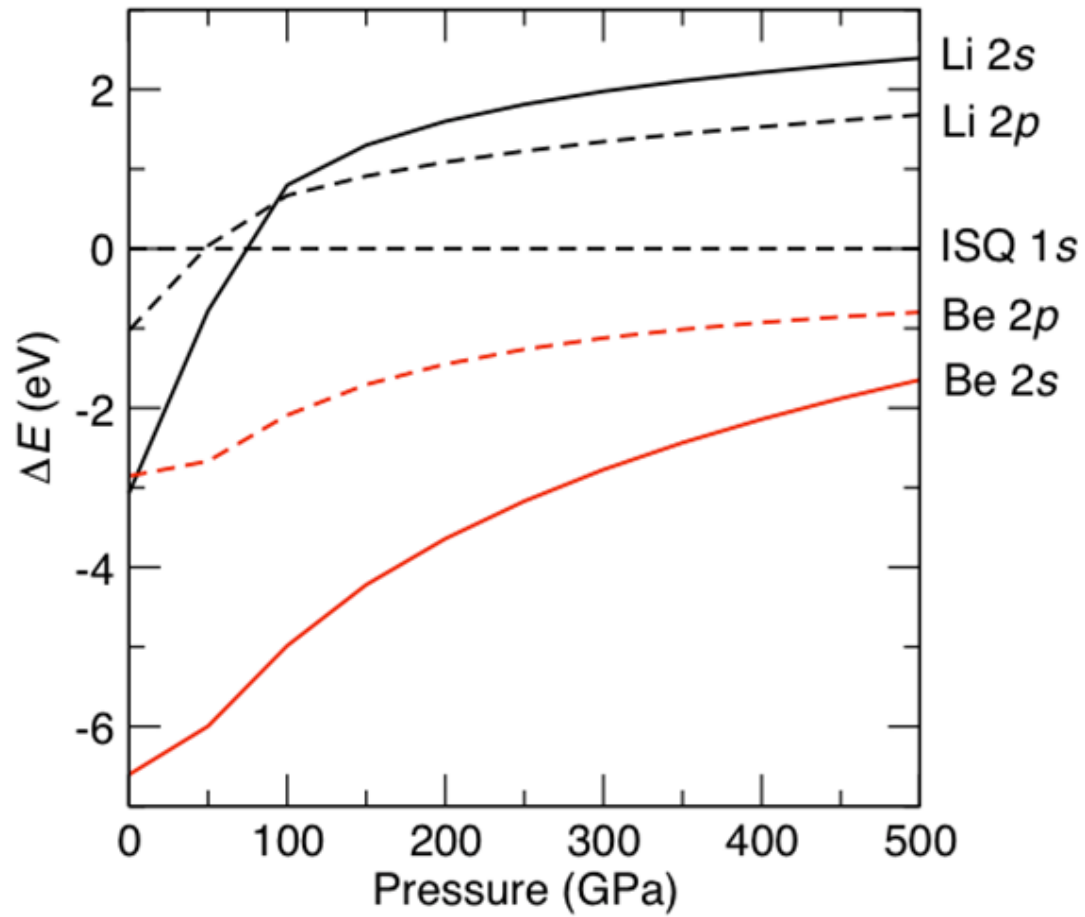


**Rule of Thumb #1** (increasing ionization potential): in general, and for elements in the same group in particular, it becomes harder to form an HPE with increasing IP of the frontier electrons.

**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.

**Note Al vs Na (same IP), Al vs B (effect of a core of same  $\ell$ )**



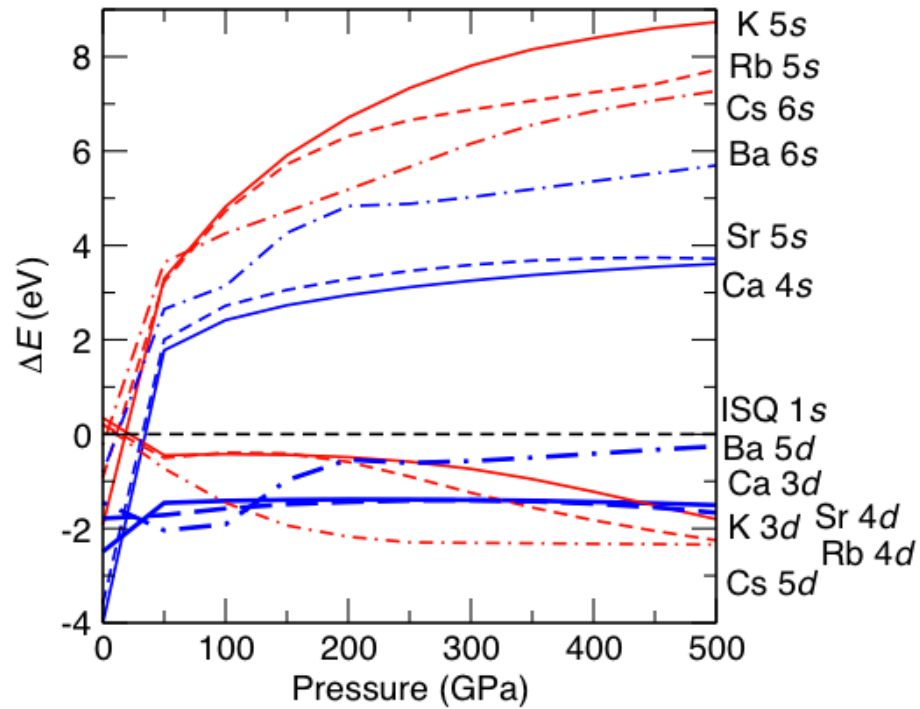


Li changes ground state configuration under pressure

## Parenthesis

Li is  $1s^2 2s^1$ , rather than  $1s^2 2p^1$  at 1 atm. Or the ground state of Li is  $^2S$  rather than  $^2P$ . This is result of electron interaction, can be traced blow by blow back to Coulomb and exchange integrals involved.

Under pressure the ground state of a Li atom goes from  $1s^2 2s^1$  to  $1s^2 2p^1$ , i.e. becomes  $^2P$ . **Pressure has the opposite effect to electron-electron interaction.**



**Increase in energy with pressure of d orbitals is less than for p is less than for s.**

Phys. Rev. 1950, 78, 235–243.

## On the Compressibility of Metallic Cesium\*

R. STERNHEIMER\*\*

*University of Chicago, Chicago, Illinois and Yale University,\*\* New Haven, Connecticut*

(Received November 1, 1949)

The volume discontinuity of cesium at 45,000 kg/cm<sup>2</sup> is attributed to a shift of the valence electrons from the 6s zone to the empty 5d zones. A Wigner-Seitz calculation for the 6s and 5d bands supports this explanation. The potential used is described and tabulated. The possible existence of similar transitions for potassium and rubidium is discussed.

P. W. Bridgman, Phys. Rev. 72, 533 (1947);

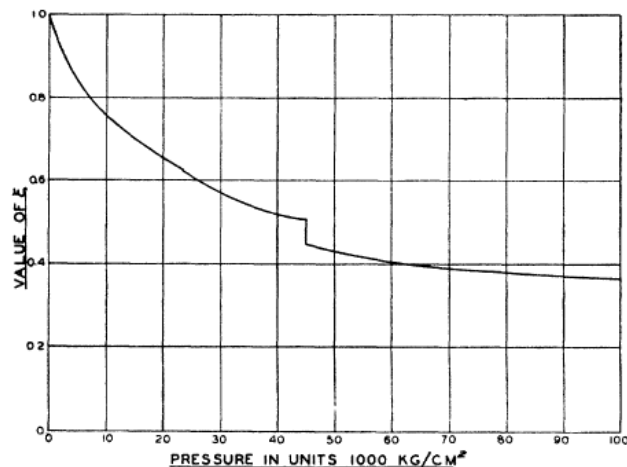
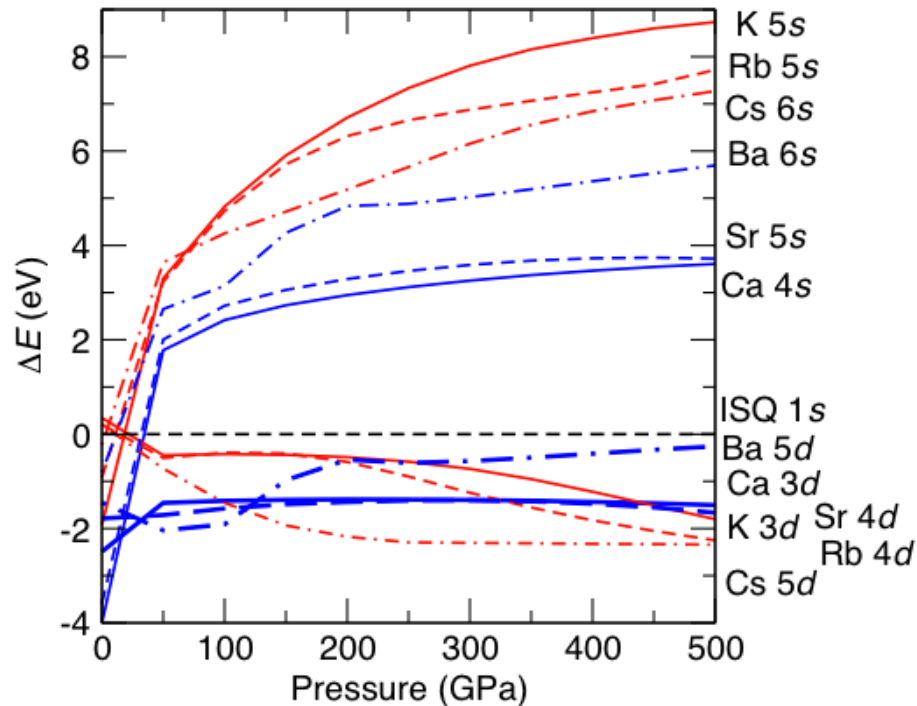


FIG. 1. Volume of cesium as a function of the pressure. The ordinate  $\xi$  is the ratio of the volume to the volume at normal pressure. (From Bridgman, reference 1.)

IN investigating the compressibility of cesium, Bridgman<sup>1</sup> found a volume discontinuity of 11 percent at 45,000 kg/cm<sup>2</sup>. Above the transition the compressibility is unexpectedly small in comparison with the other alkalis and decreases abnormally rapidly with increasing pressure. Figure 1 shows the volume as a function of the pressure.

In order to explain the phase transition, Fermi proposed that the valence electron is forced into a vacant internal orbit. This hypothesis is suggested by the large volume change and the proximity of cesium to the rare earths. The two available orbits are 4f and 5d.



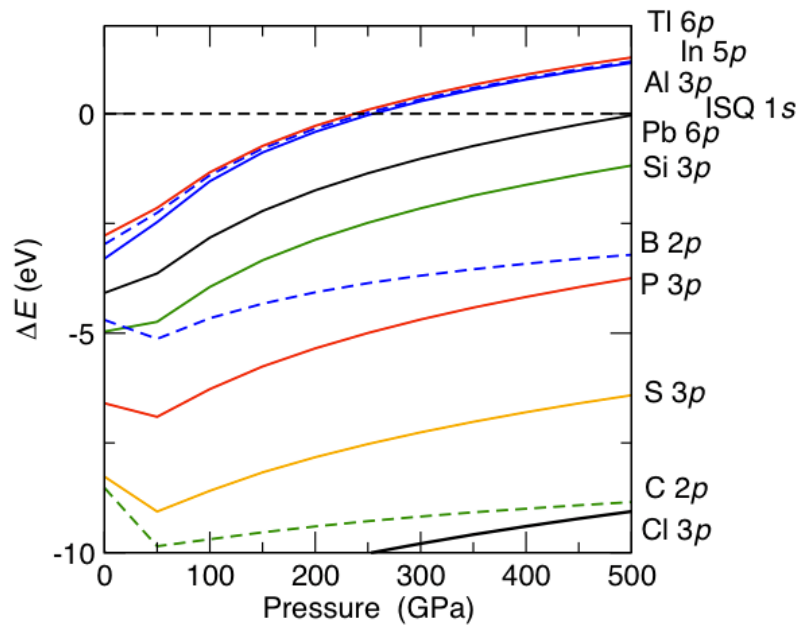
**Increase in energy with pressure of d orbitals is less than p is less than s.**

**Rule of Thumb #3** (effect of d orbitals): Slopes of orbitals with pressure go as  $d < p < s$ . 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 IP's – as pressure is applied, their s electrons will transfer to the next available d orbitals.

For other configurational changes with compression

**Squeezing All Elements in the Periodic Table: Electron Configuration and Electronegativity of the Atoms under Compression**, Martin Rahm, Roberto Cammi, N. W. Ashcroft, Roald Hoffmann, J. Amer. Chem. Soc. 141, 10253-10271 (2019).

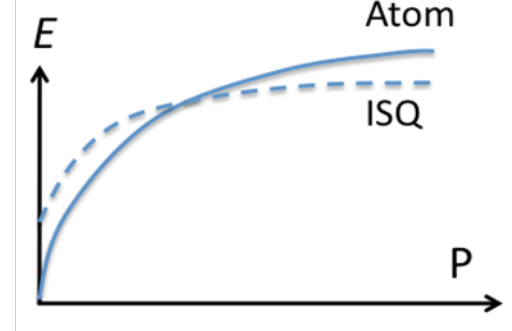
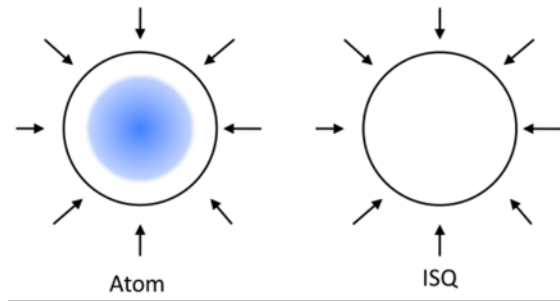
Lots of fun in the lanthanides....



Note C vs Si (core)

Prediction : TI, In will form HPEs

.



ISQ = Interstitial Quasi-Atom

**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.

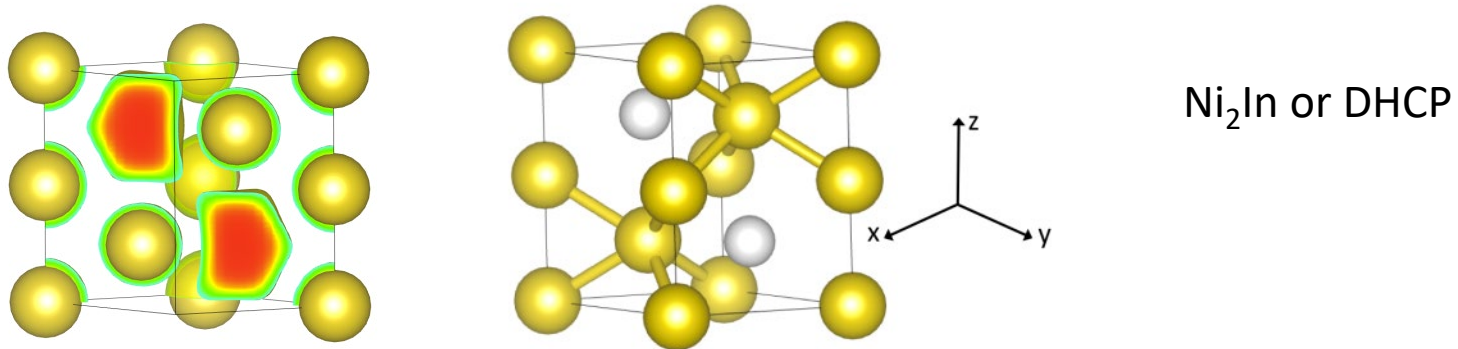
**Rule of Thumb #2:** (effect of incompressible core): ISQ formation is more likely when the valence electrons, s or p, move around a relatively incompressible core. For example, it is easier for Al and Mg to form HPEs than B and Be. This is also why Li and Na form HPEs readily.

**Note Al vs Na (same IP), Al vs B (effect of a core of same  $\ell$ )**

**Rule of Thumb #3** (effect of d orbitals): Slopes of orbitals with pressure go as  $d < p < s$ . 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 IP's – as pressure is applied, their s electrons will transfer to the next available d orbitals.



# Electrides as anions



*The **Na HPE** structure at 200 GPa. The yellow balls show the position of the Na cores, the lines are nearest neighbor contacts. The white balls indicate the centers of the ISQs.*

Ma, Y.; Eremets, M.; Oganov, A. R.; Xie, Y.; Trojan, I.; Medvedev, S.; Lyakhov, A. O.; Valle, M.; Prakapenka, V. Transparent Dense Sodium. *Nature* **2009**, *458*, 182-185.

Lazicki, A.; Goncharov, A. F.; Struzhkin, V. V.; Cohen, R. E.; Liu, Z.; Gregoryanz, E.; Guillaume, C.; Mao, H. K.; Hemley, R. J. Anomalous Optical and Electronic Properties of Dense Sodium. *Proc. Nat. Acad. Sci. U.S.A.* **2009**, *106*, 6525-6528.

## That electron density of atoms (under conditions of high pressure) has the structural consequences of real ions is not new to us:

U. Schwarz, Metallic high-pressure modifications of main group elements, *Z. Kristall.* 219, 376-390 (2004)

Maksimov, E. G.; Magnitskaya, M. V.; Fortov, V. E. Non-simple Behavior of Simple Metals at High Pressure. *Physics – Uspekhi* **2005**, 48, 761–780.

Pickard, C. J.; Needs, R. J. Dense Low-Coordination Phases of Lithium. *Phys. Rev. Lett.* **2009**, 102, 146401

Ma, Y.; Eremets, M.; Oganov, A. R.; Xie, Y.; Trojan, I.; Medvedev, S.; Lyakhov, A. O.; Valle, M.; Prakapenka, V. Transparent Dense Sodium. *Nature* **2009**, 458, 182-185

Pickard, C. J.; Needs, R. J. Aluminium at Terapascal Pressures. *Nat. Mat.* **2010**, 9, 624-627.

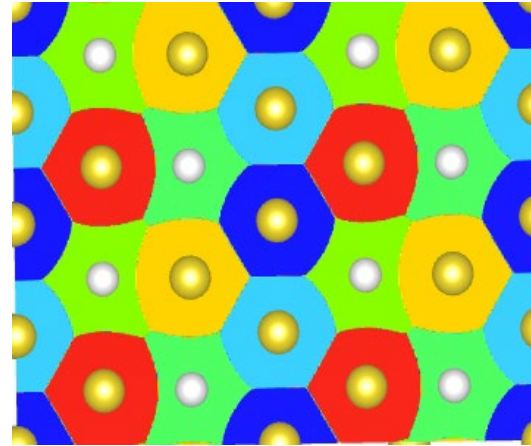
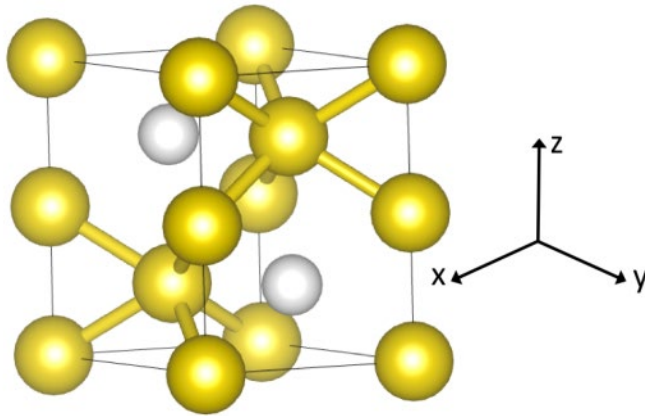
Pickard, C. J.; Needs, R. J. Predicted Pressure-Induced s-Band Ferromagnetism in Alkali Metals. *Phys. Rev. Lett.* **2011**, 107, 087201.

Martinez-Canales, M.; Pickard, C. J.; Needs, R. J. Thermodynamically Stable Phases of Carbon at Multiterapascal Pressures. *Phys. Rev. Lett.* **2012**, 108, 045704.

Dong, X.; Oganov, A. R.; Goncharov, A. F.; Stavrou, E.; Lobanov, S.; Saleh, G.; Qian, G.-R.; Zhu, Q.; Gatti, C.; Deringer, V.L.; Dronskowski, R. Zhou, X.-F.; Prakapenka, V.; Konôpková, Z.; Popov I.A., Boldyrev A. I. Wang, H.-T. Stable Compound of Helium and Sodium at High Pressure. **Nature Chemistry** **9**, 440-445 (2017)

Ángel Vegas, **Structural Models of Inorganic Crystals. From the Elements to the Compounds**. Editorial Universitat Politècnica de València. 2017: `...valence electrons can separate in the solids in the form of non-nuclear maxima (NNM) that are located at the same position occupied by the O/S atoms in the corresponding oxides/sulfides!

## QTAIM or Bader basins and charges



Red, blue, yellow = Na<sup>+</sup>; green = ISQ<sup>-</sup>

Charge in electrone basin

on Cl in NaCl

on O in MgO

-0.80 at 100 Gpa

-1.12 above 200 Gpa

-0.78 at 1 atm

-1.74

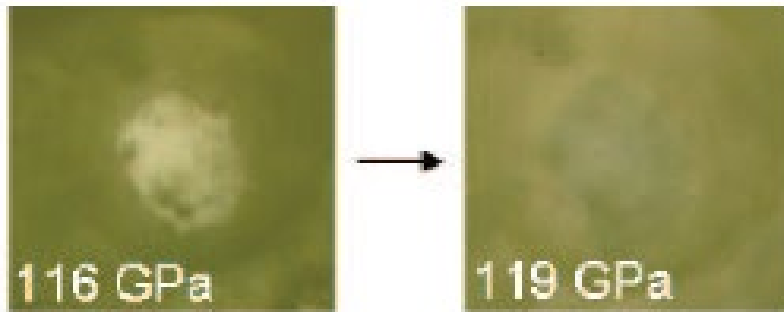
A direct comparison with inorganic molecules is possible

**Na<sub>2</sub>E, E = O, S, Se** antifluorite structure at P = 1 atm  
Ni<sub>2</sub>In structure at 16 GPa (Syassen et al)

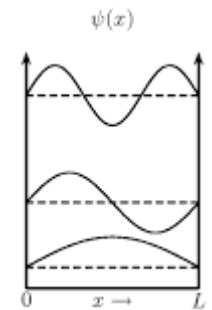
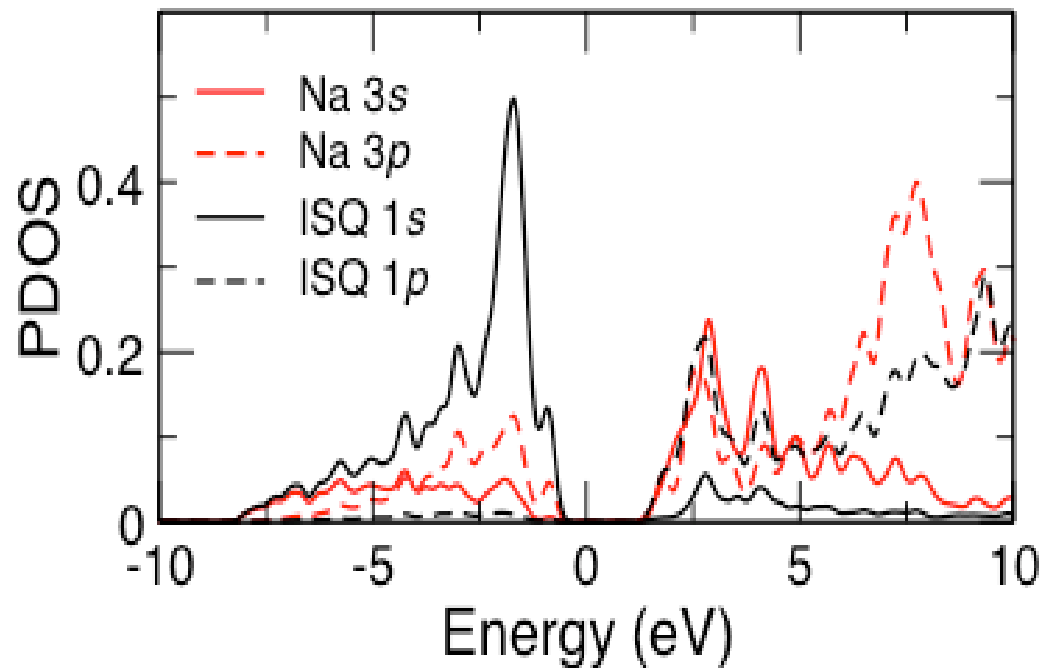
	Bader Charge of anion or ISQ (a.u.)	Na <sup>+</sup> volume Å <sup>3</sup>	Anion or ISQ volume Å <sup>3</sup>
Na HPE 300 GPa	-1.12	4.86	3.58
Na <sub>2</sub> S 16 GPa	-1.44	6.32	19.72
Na <sub>2</sub> S 300 GPa	-1.38	4.45	12.64
Na <sub>2</sub> Se 300 GPa	-1.32	4.52	14.15

ISQ is much smaller than an S<sup>2-</sup>; it's about the size of an Na<sup>+</sup>  
(similar findings by Dong, Oganov, Goncharov et al in Na<sub>2</sub>He)

There is a high **density** of charge on an ISQ. Consequences?

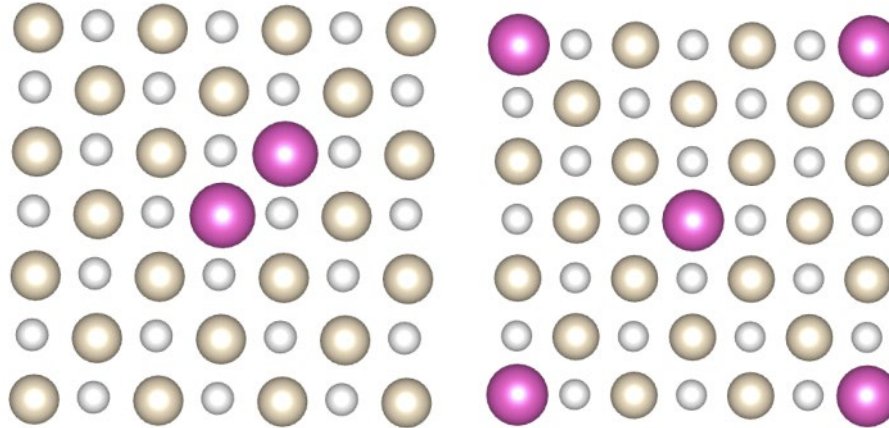


Lazicki, A.; Goncharov, A. F.;  
 Struzhkin, V. V.; Cohen, R. E.; Liu,  
 Z.; Gregoryanz, E.; Guillaume, C.;  
 Mao, H. K.; Hemley, R. J.  
 Anomalous Optical and Electronic  
 Properties of Dense Sodium. *Proc.  
 Nat. Acad. Sci. U.S.A.* **2009**, *106*,  
 6525-6528

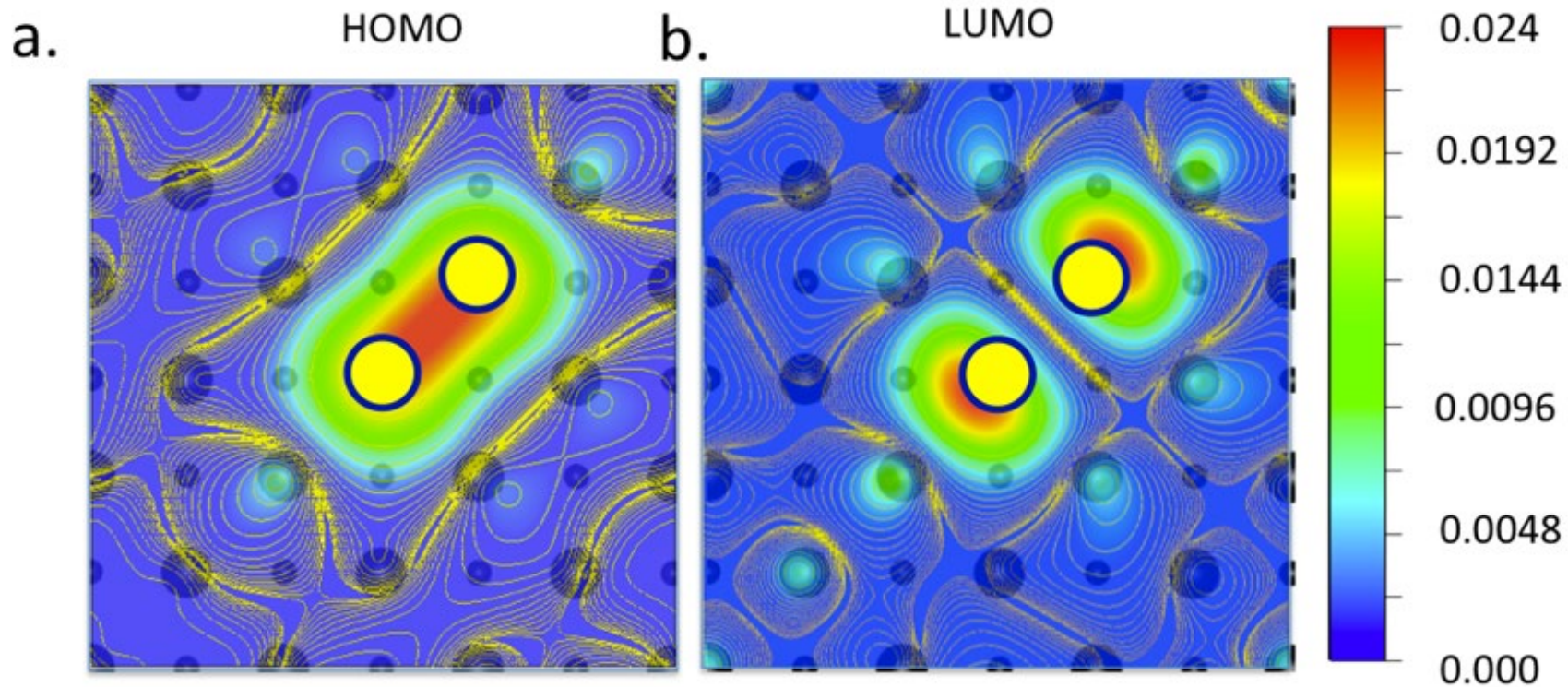


*The projected density of states of HPE Na at 300 GPa. Conduction band is ISQ 1p!  
 Possible relation to color of sodium-ammonia solutions...*

# Chemical bonds between ISQs put two ISQs in He compression chamber

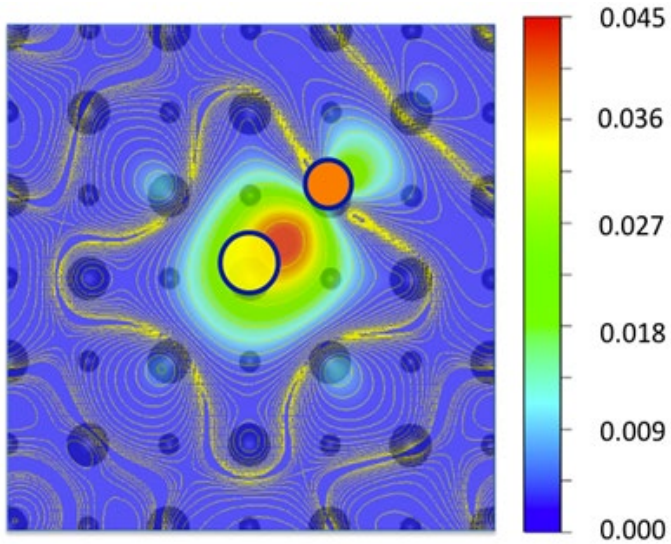


Pressure	E-E (Å)	E.....E (Å)
100 GPa	1.70	5.10
500	1.39	4.17



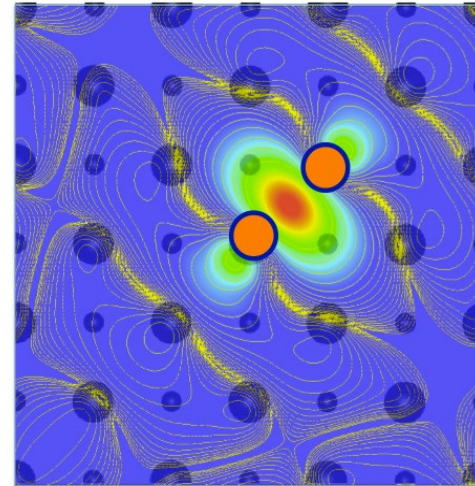
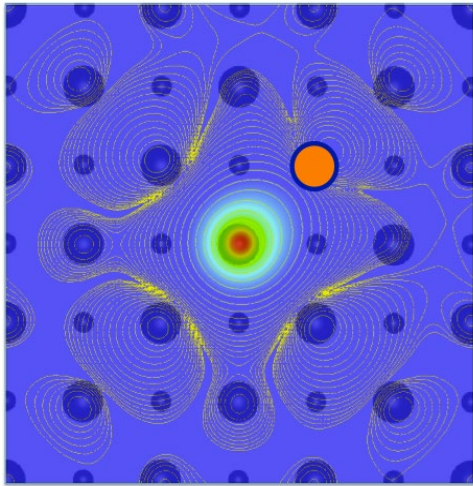
*The calculated density (in unit of electrons/bohr<sup>3</sup>) of the a) HOMO and b) LUMO of an E-E quasimolecule in the He lattice model, at a minimal ISQ separation of 1.70 Å, at 100 GPa. Small grey spheres represent the position of He atoms in the lattice*

**E-Li**



*Calculated electron density of an E-Li QM in the He lattice model at 100 GPa. The large light sphere at the center and the medium sphere with orange fill show the positions of the ISQ (E) and the Li atom, respectively.*

**H-Li**

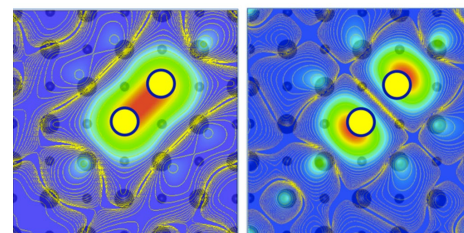
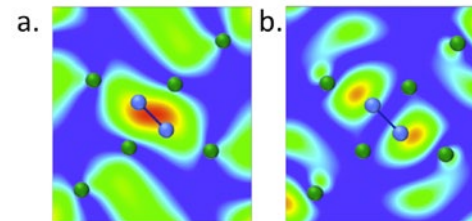
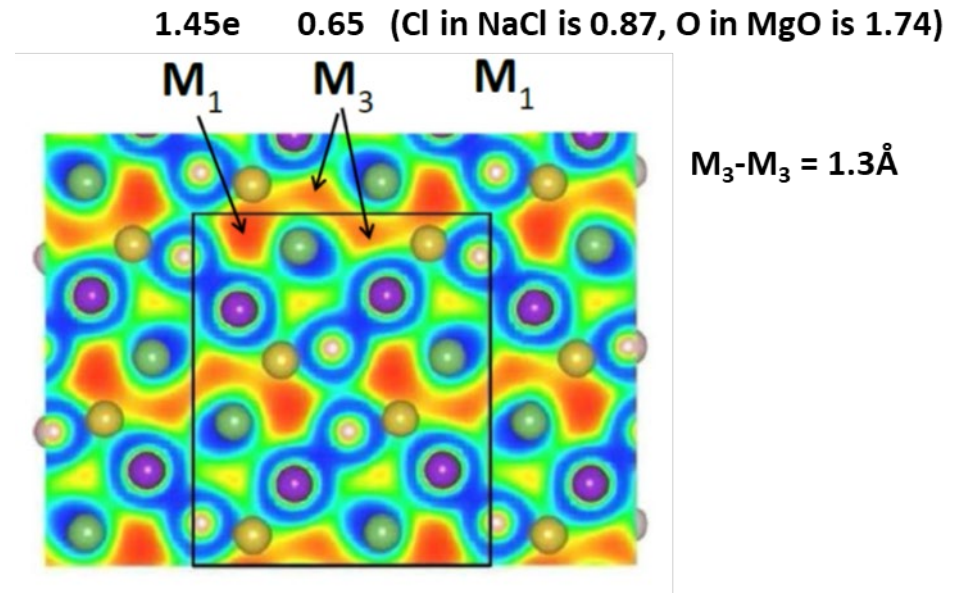
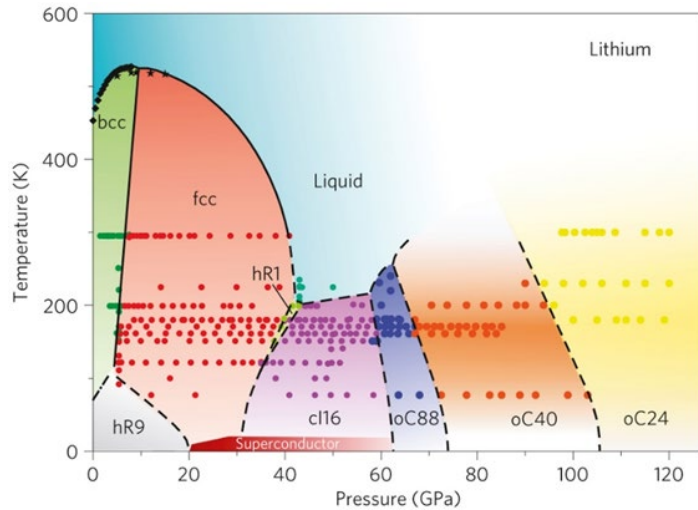


**Li-Li**

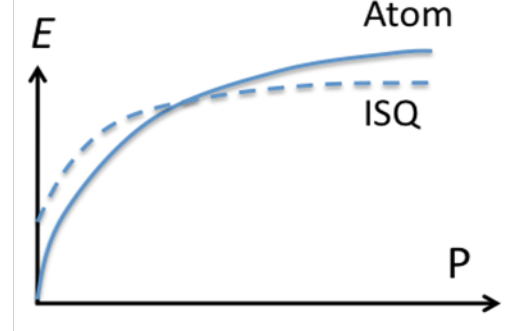
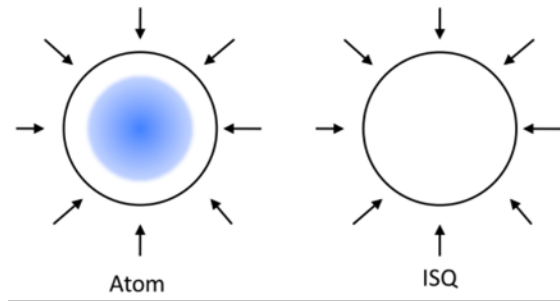
*a) Li-H, and b) Li<sub>2</sub> in the 106-He-atom compression chamber at 100 GPa. The large spheres with orange fill show the position of Li atoms. The H atom at left is at the center of the red electron density maximum in the contour plot.*



# A quasimolecule in semiconducting oC40, Aba2 Li?



Quasimolecules in Compressed Lithium. *M. Miao, R. Hoffmann, I. Naumov, and R. Hemley. Angew. Chem. Int. Ed. 56, 972-975 (2017).*



ISQ = Interstitial Quasi-Atom

**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.

**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.

**Note Al vs Na (same IP), Al vs B (effect of a core of same  $\ell$ )**

**Rule of Thumb #3** (effect of d orbitals): Slopes of orbitals with pressure go as  $d < p < s$ . 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 IP's – as pressure is applied, their s electrons will transfer to the next available d orbitals.

General electrone problem



The electrons have a choice:

1. Go into antibonding MOs of A or AB frameworks. This will show up in weakened bonds.
2. Go into Rydberg orbitals (higher principal quantum number orbitals) of A or AB. For, Li 3s or 3p...
3. Reduce (make neutral) some of the cations, leading to formation of regions of metallic A, interspersed with regions of ionic bonding.
4. Stay in space between nuclei. That space is “quantized”.

The choice is not obvious

# High Pressure Electrides: A Chemical and Physical Theory

*Mao-sheng Miao and Roald Hoffmann*

Beijing Computational Science Research Center, Beijing 10084, P. R. China and Department of Physics,  
California State University Northridge, CA 91330, USA  
Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

**Accts. Chem. Res. 2014, 47, 1311–1317**  
**J. Amer. Chem. Soc. 2015, 137, 3631-3637**  
**Angew. Chem. Int. Ed. 2017, 56, 972-075**



M.S.M. is supported by the MRSEC program (NSF-DMR1121053) and the ConvEne-IGERT Program (NSF-DGE 0801627). He acknowledges gratefully the NSF-funded XSEDE resources (TG-DMR130005).