High Pressure Electrides: A Predictive Chemical and Physical Theory

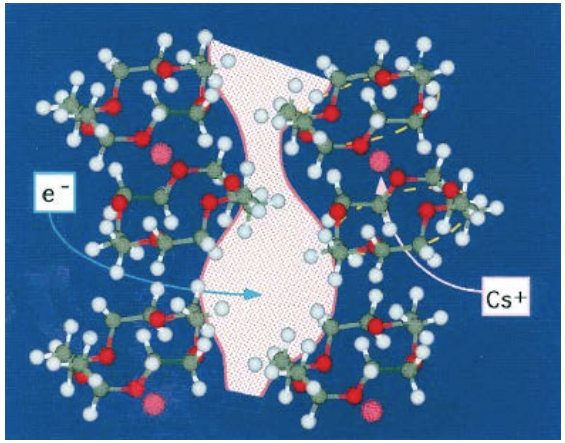
Mao-sheng Miao and Roald Hoffmann

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

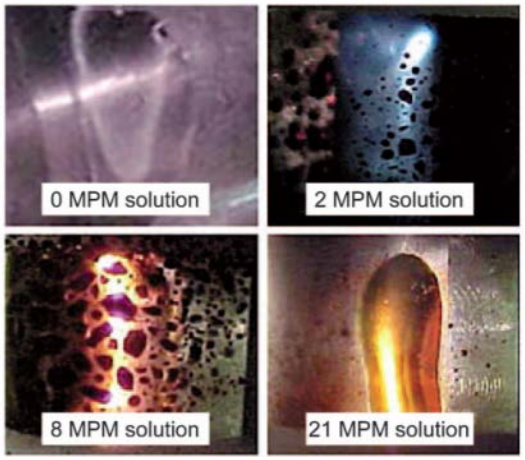
Accts. Chem. Res. 2014, 47, 1311−1317
and to be published

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).

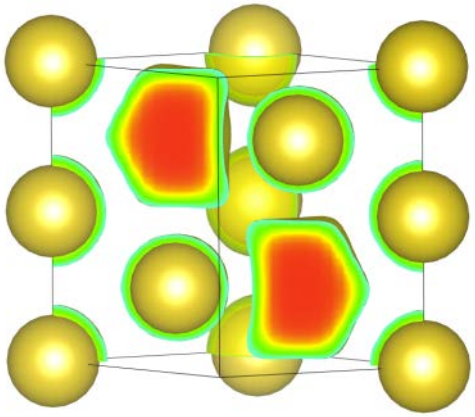
Electrides, at ambient and high pressure



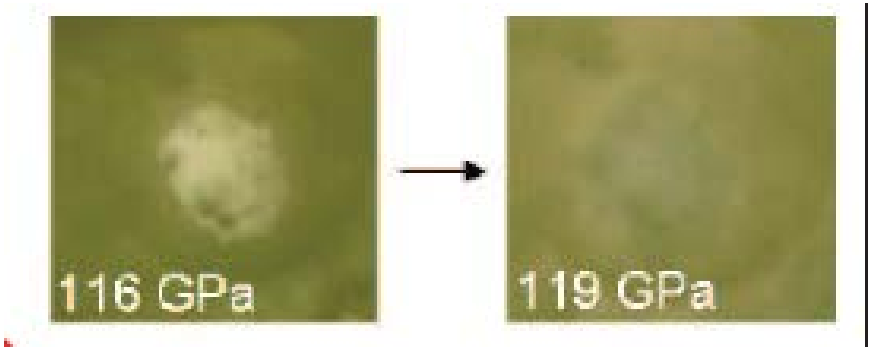
Jim Dye, Acc. Chem. Res. ***42,*** *1564 (2009).*



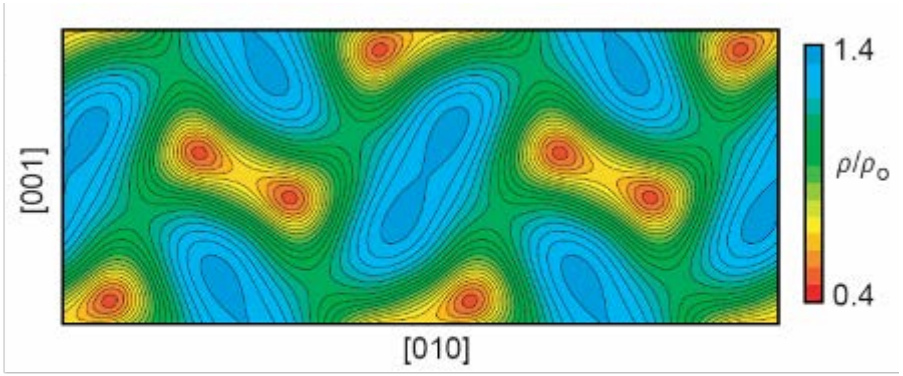
Alkali metal ammonia solutions



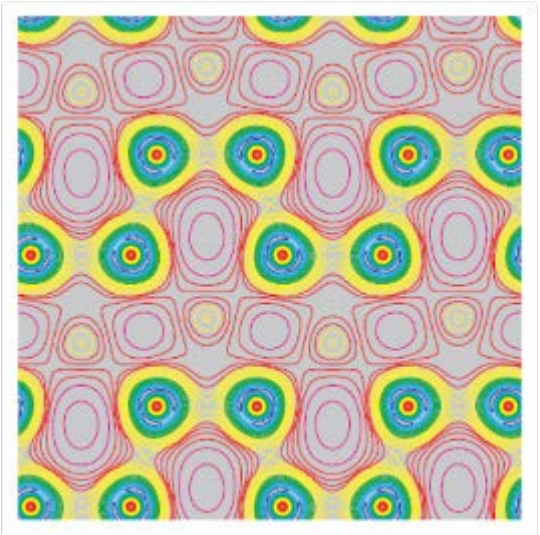
Ma, Y.; Eremets, M.; Oganov, A. R.; Xie, Y.; Trojan, I.; Medvedev, S.; Lyakhov, A. O.; Valle, M.; Prakapenka, V. Transparent Dense Sodium. Nature 2009, 458, 182−U183.



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

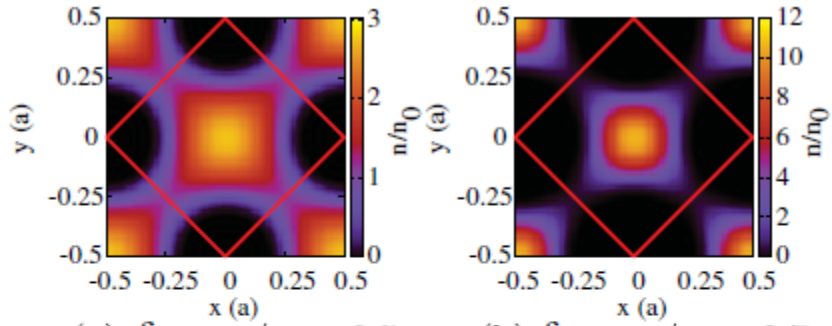


Elemental Li

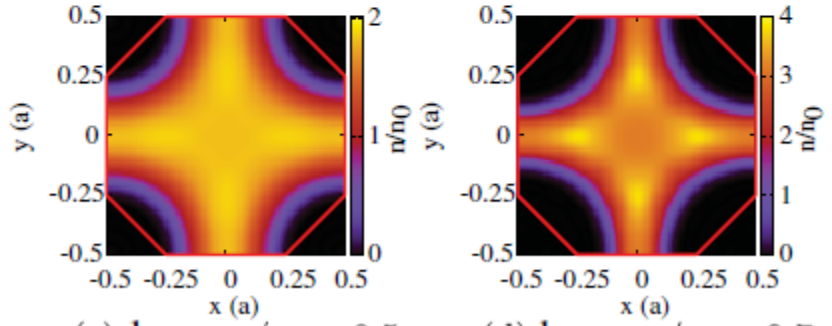


top: Neaton, J. B.; Ashcroft, N. W. Pairing in Dense Lithium. *Nature* 1999, *400*, 141-144.
bottom: Nelmes group 2003

Rousseau, B.; Ashcroft, N. W. Interstitial Electron Localization, *Phys. Rev. Lett.* 2008, 101, 046407.

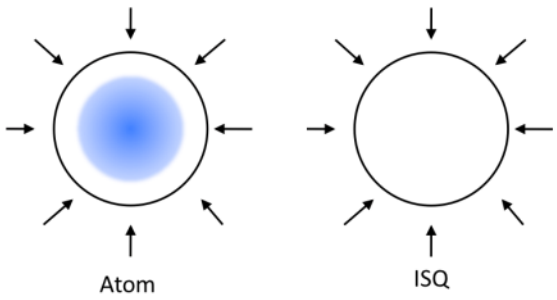


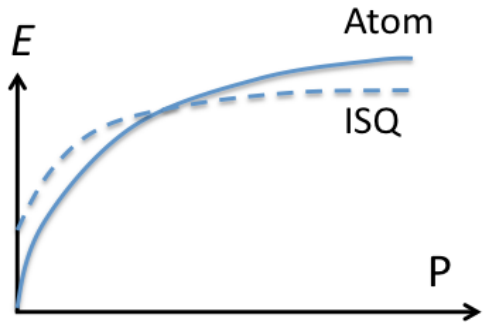
(a) fcc: $r_c/r_s = 0.5$ (b) fcc: $r_c/r_s = 0.7$



(c) bcc: $r_c/r_s = 0.5$ (d) bcc: $r_c/r_s = 0.7$

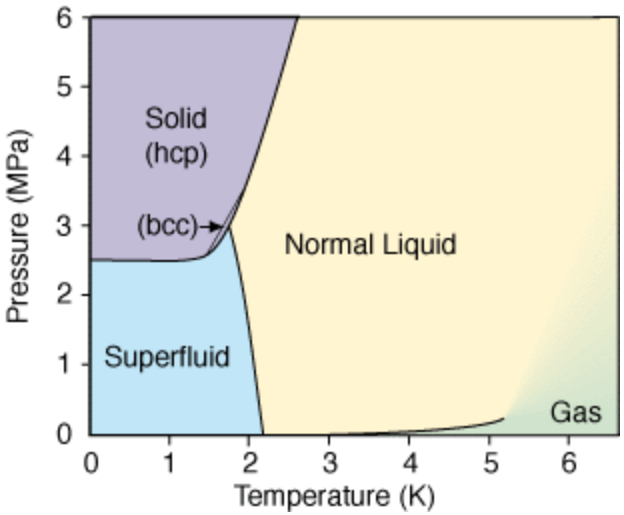
We investigate the ground-state properties of a collection of N noninteracting electrons in a macroscopic volume Ω also containing a crystalline array of N spheres of radius r_c, each taken as largely impenetrable to electrons and with proximity of neighboring excluding regions playing a key physical role. The sole parameter of this quantum system is the ratio r_c/r_s, where r_s is the Wigner-Seitz radius. Two lattices (fcc and bcc) are selected to illustrate the behavior of the system as a function of r_c/r_s. As this ratio increases valence electrons localize in the interstitial regions and the relative bandwidth ϵ_F/ϵ_F^0 is found to decrease monotonically for both. The system is motivated by the behavior of the alkali metals at significant compression. It accounts for band narrowing, leads to electronic densities with interstitially centered maxima, and can be taken as a model which may be improved upon by perturbation and other methods.

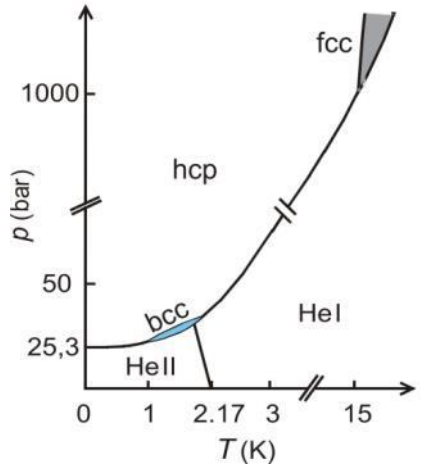


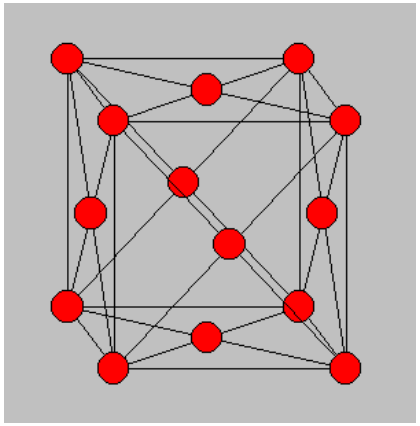


ISQ = Interstitial Quasi-Atom

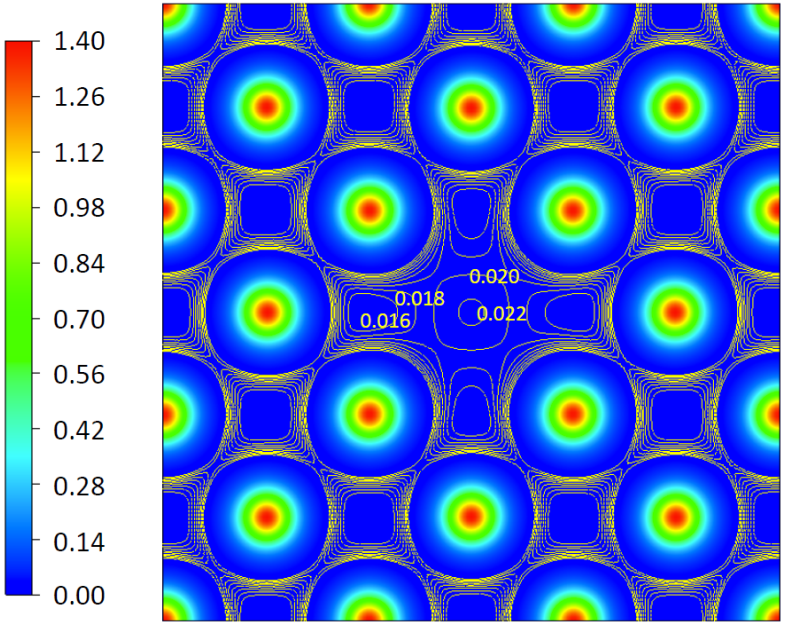
He compression model

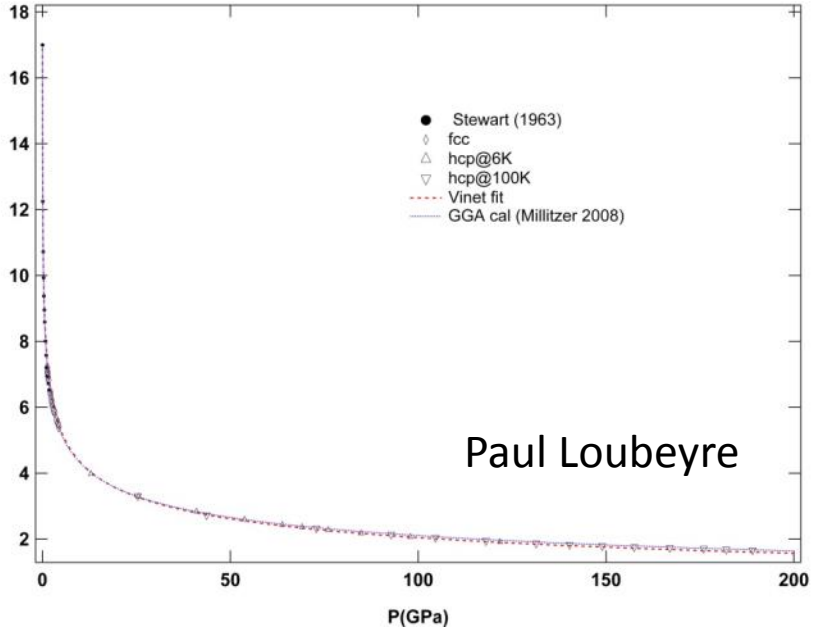






108 atom fcc model = 3 x 3 x3 nonprimitive cell

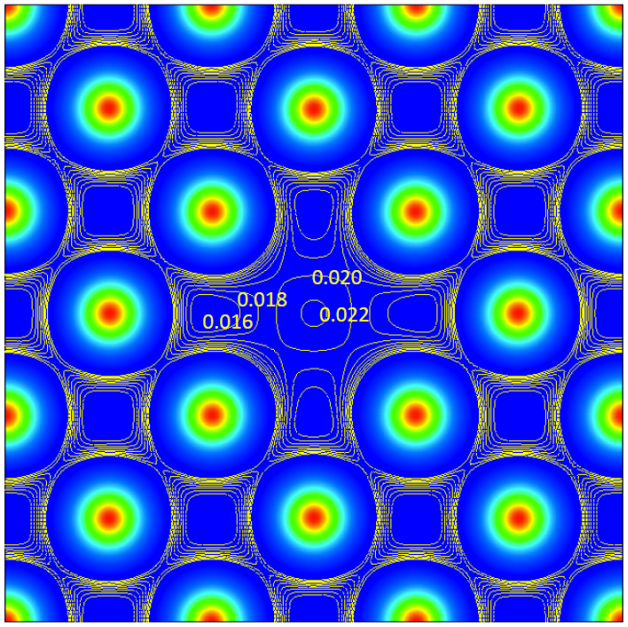


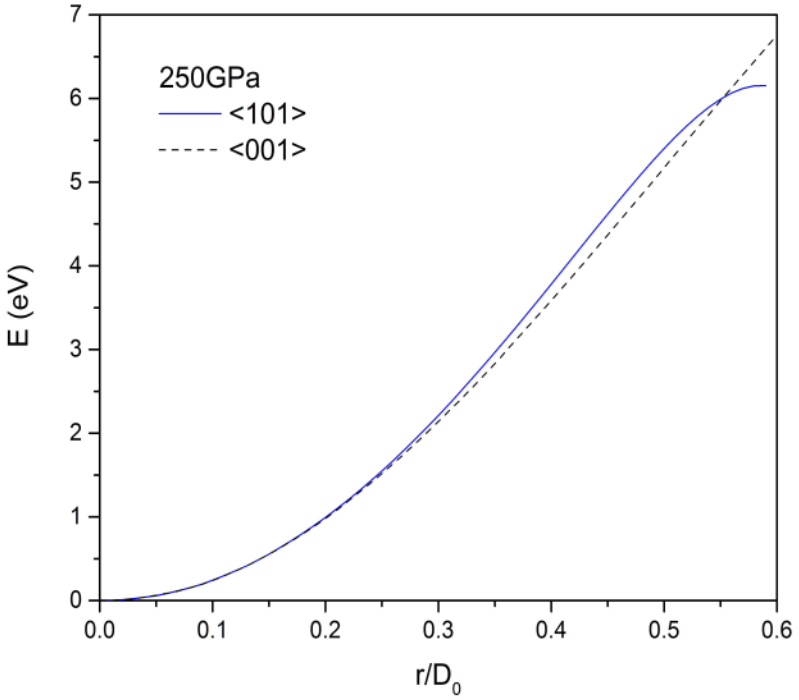


Constrained compression, keeping O_h symmetry

Pressure (GPa)	D_0 108 He (Å)	D_r, 107 He (Å)	D_r 107 He + e (Å)
0.0001	2.87	2.87	3.49
1	2.57	2.56	3.23
10	2.16	2.10	2.34
50	1.84	1.78	1.83
100	1.70	1.64	1.67
200	1.56	1.51	1.53
300	1.48	1.43	1.45
400	1.43	1.38	1.39
500	1.39	1.34	1.35

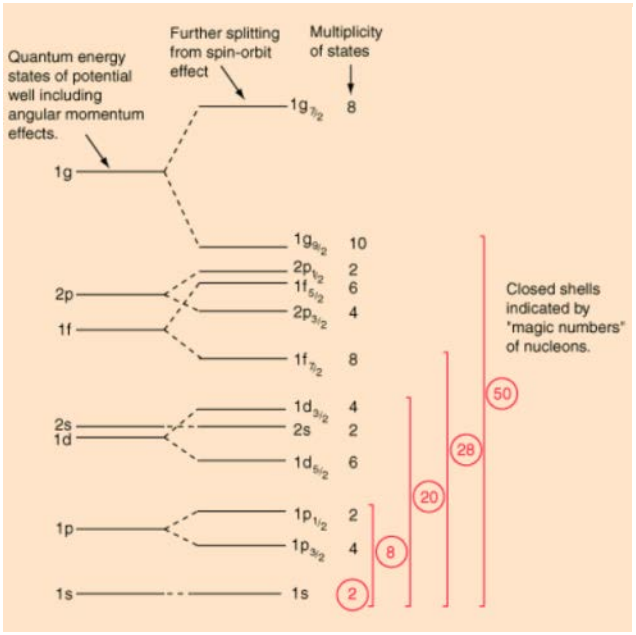
15 Å bubbles in liquid He!

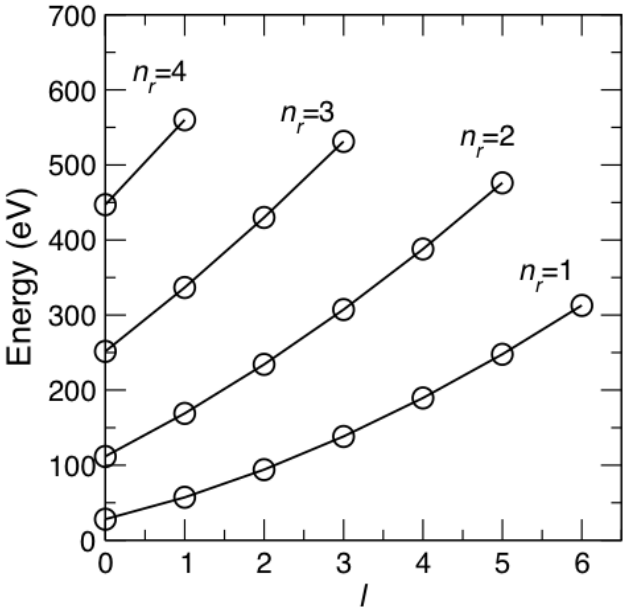


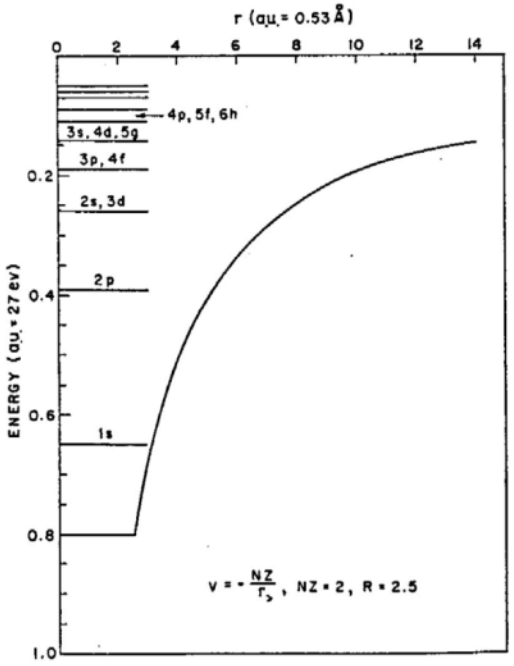


Potential for electron + He atom comes from Study of the Properties of an Excess Electron in Liquid Helium. I. The Nature of the Electron—Helium Interactions, Joshua Jortner, Neil R. Kestner, Stuart A. Rice, and Morrel H. Cohen, J. Chem. Phys. 43, 2614-2625 (1965).

Energy E of an electron moving along the (1,0,1) (directly at a surrounding He) and (1,0,0) (toward the four-fold "hole") directions of a cube-octahedron (He's located at $(D_0/\sqrt{2})(\pm1, \pm1, 0)$, $(\pm1, 0, \pm1)$, $(0, \pm1, \pm1)$) 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.







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

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

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

1s < 1p <1d ~ 2s

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

under pressure, radial nodes hurt…

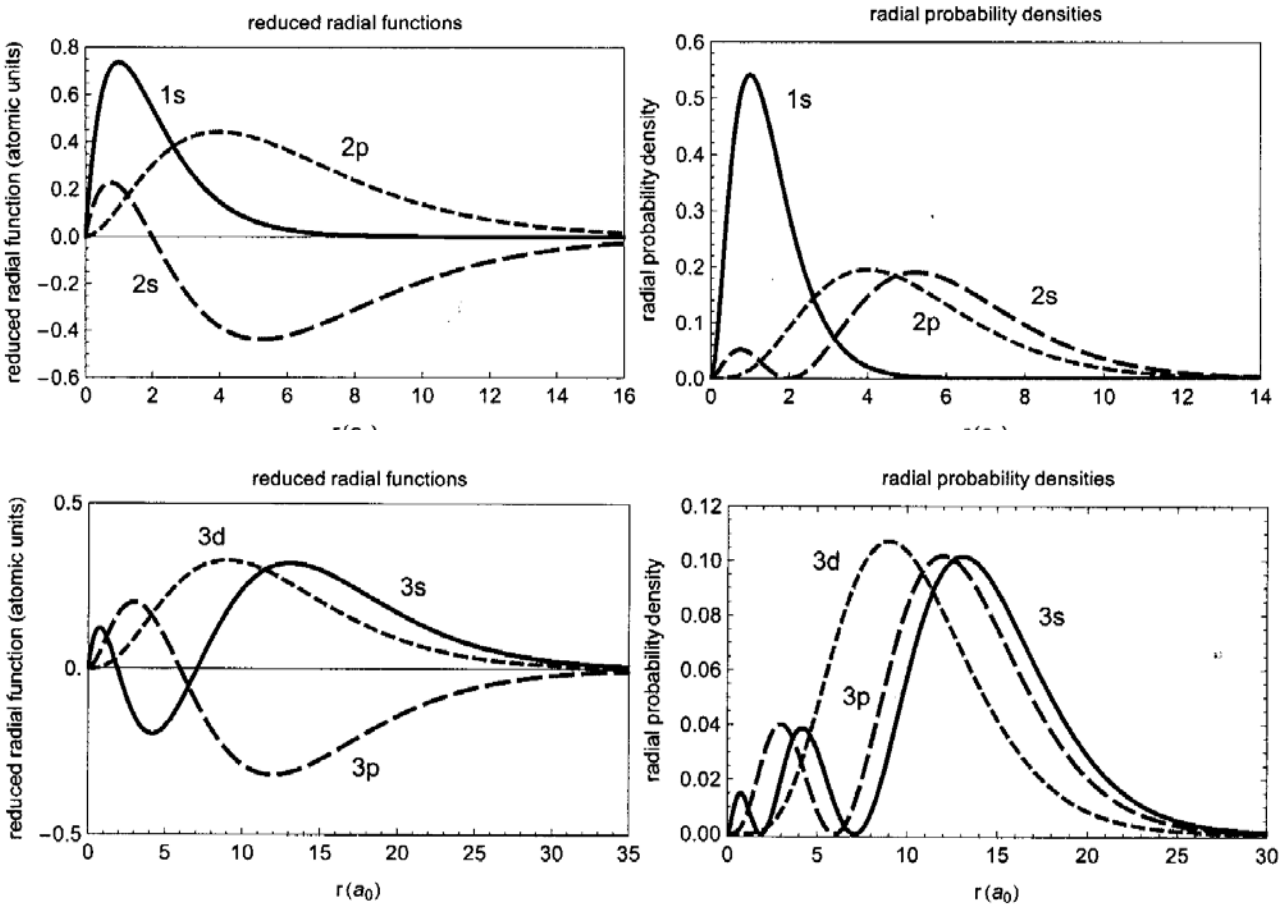
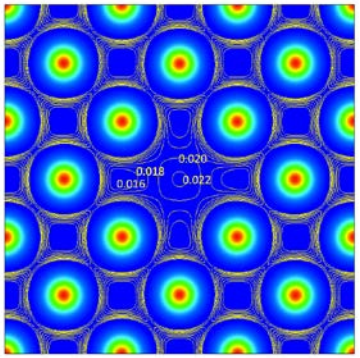


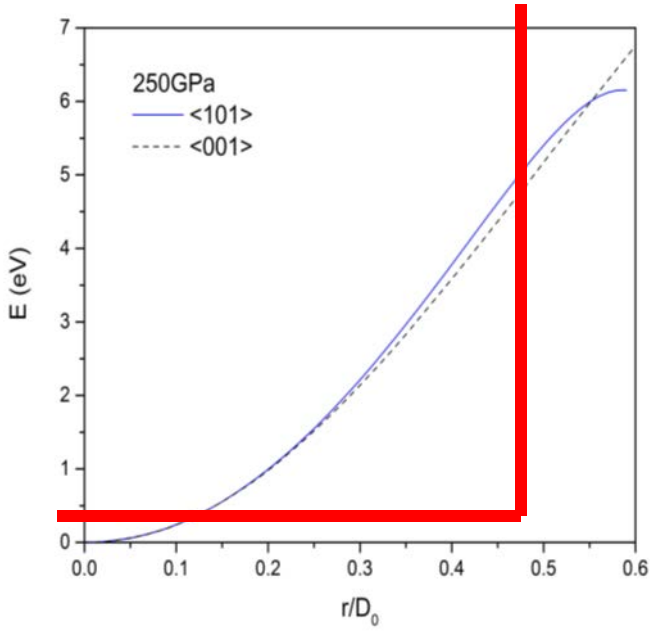
FIGURE 5.3. *Reduced radial functions (upper panel) and radial probability densities (lower panel) for the $n = 3$ states of atomic hydrogen.*

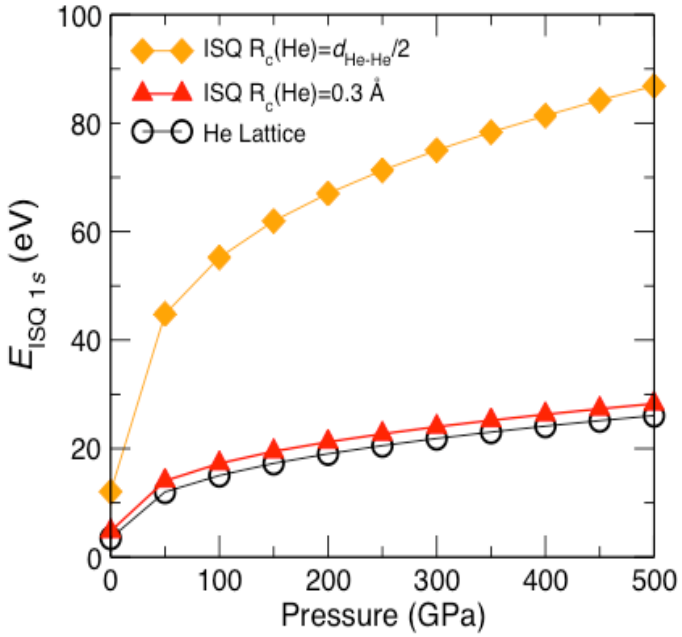
Or… start from a hydrogenic atom 1s < 2s=2p < 3s=3p=3d

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**

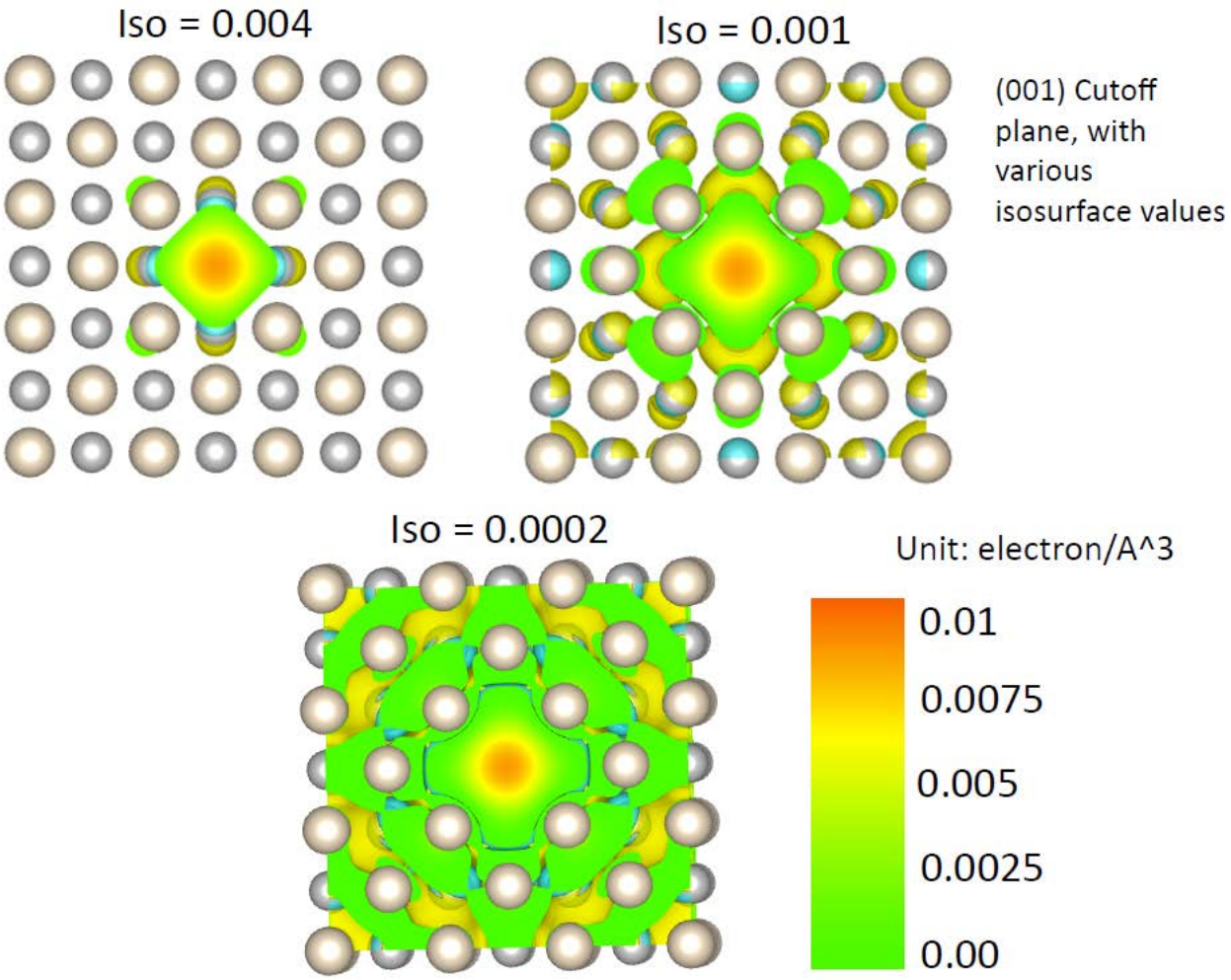


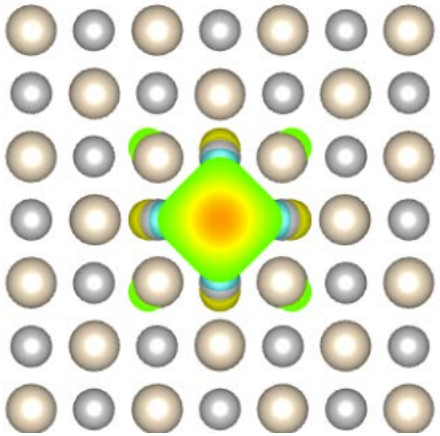


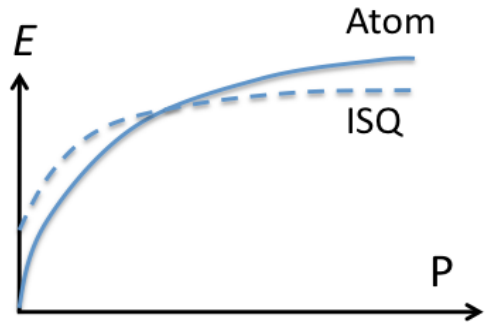


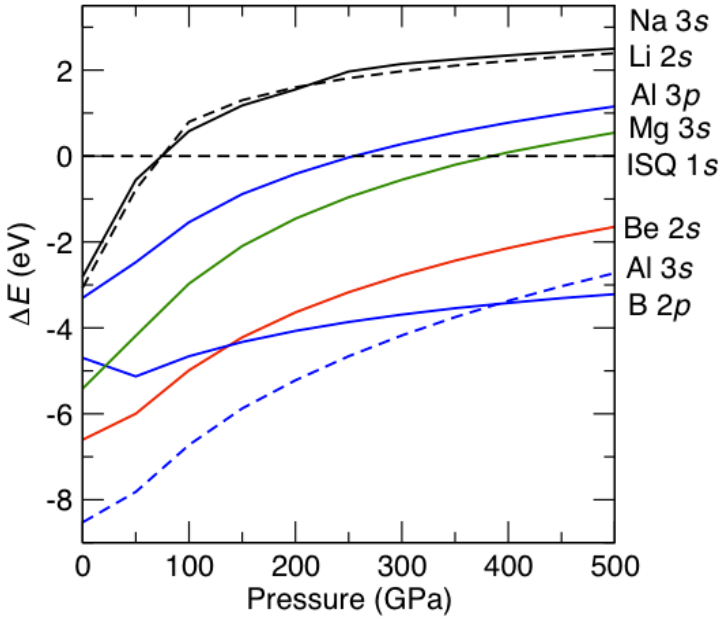
Comparing the 1s orbital energies from FCC He model with the particle in a box model at various assumed values of the radius of the containing sphere, $R = D_0 - R_c$. For the orange line, the radius reduction R_c is taken is taken as the half of the He-He distance in FCC. The red line is the best fit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

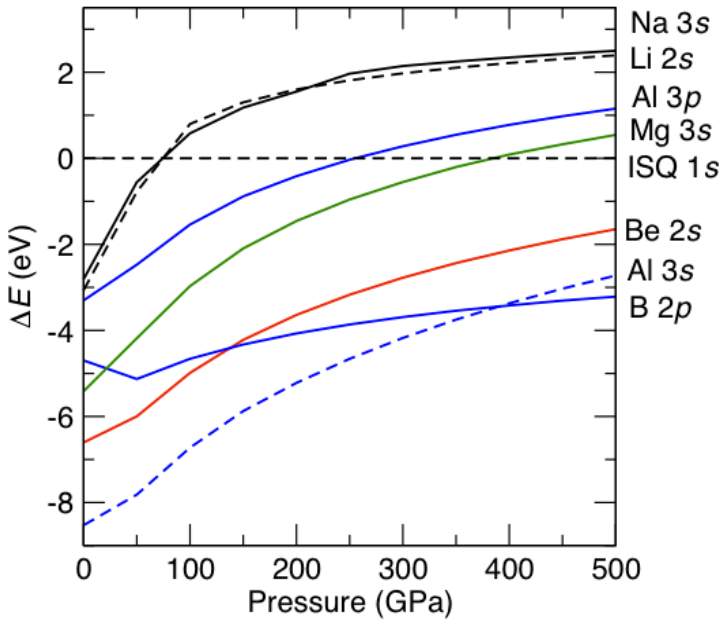
the ISQ 1s level

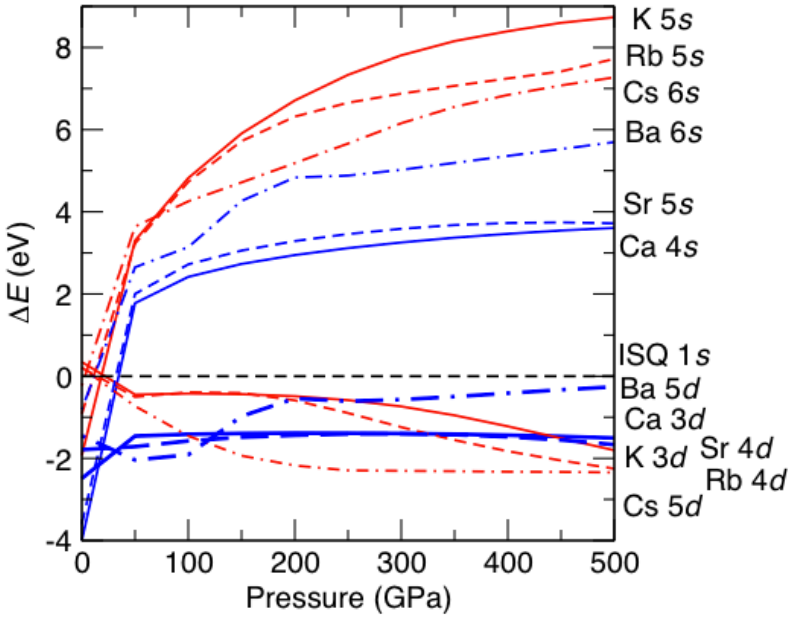





E
Atom
ISQ
P


Na 3s
Li 2s
Al 3p
Mg 3s
ISQ 1s
Be 2s
Al 3s
B 2p
ΔE (eV)
2
0
-2
-4
-6
-8
0
100
200
300
400
500
Pressure (GPa)

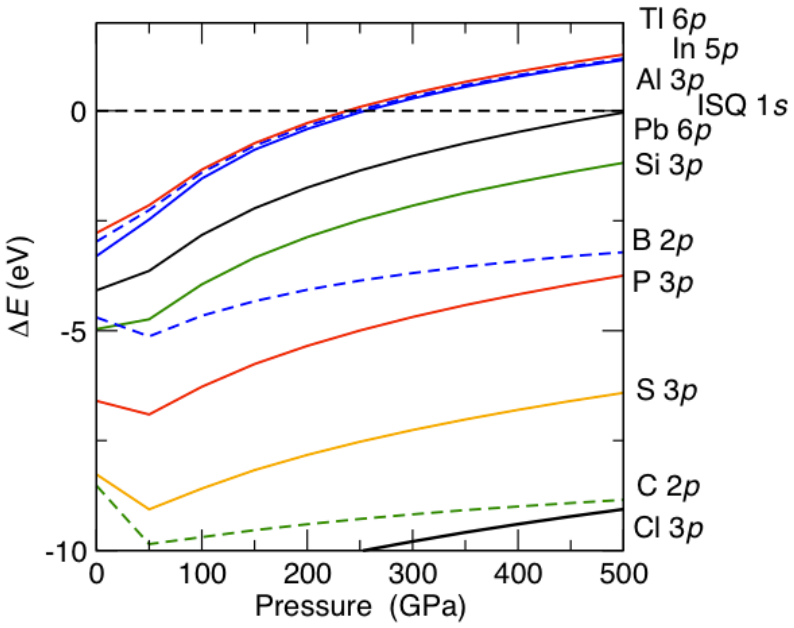


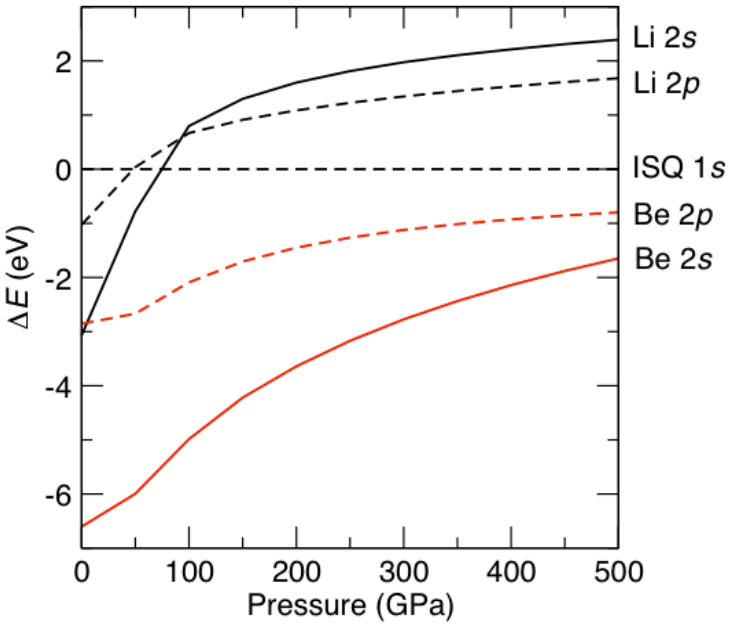


Important: Increase in energy with pressure of d orbitals is less than p is less than s.

K, Ca under pressure become d-metals. **Explanation first provided in Sternheimer, R. On the Compressibility of Metallic Cesium. *Phys. Rev.* 1950, *78*, 235-243. With a credit to Enrico Fermi for suggesting it!**

Note Al vs Na (same IP), Al vs B (effect of a core of same ℓ)





Note C vs Si (core)

Prediction : Tl, In will form HPEs

Li (Be): at high enough pressure 2p will come below 2s.

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.

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.

High Pressure Electrides
The Chemical Nature of Interstitial Quasiatoms

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

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

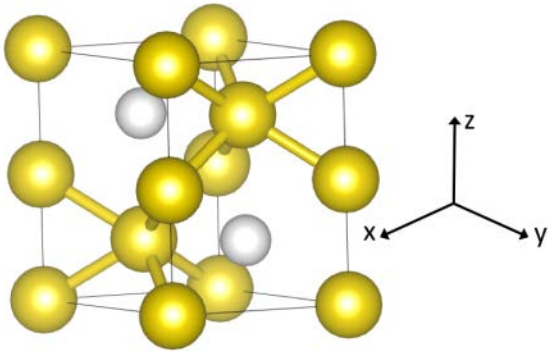
Pickard, C. J.; Needs, R. J. Aluminium at Terapascal Pressures. *Nat. Mat.* **2010**, *9*, 624-627.

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.; Zhou, X.-F.; Prakapenka, V.; Konôpková, Z.; Wang, H.-T. Stable Compound of Helium and Sodium at High Pressure. **2014**, arXiv 1309.3827v3.

Electrides as anions

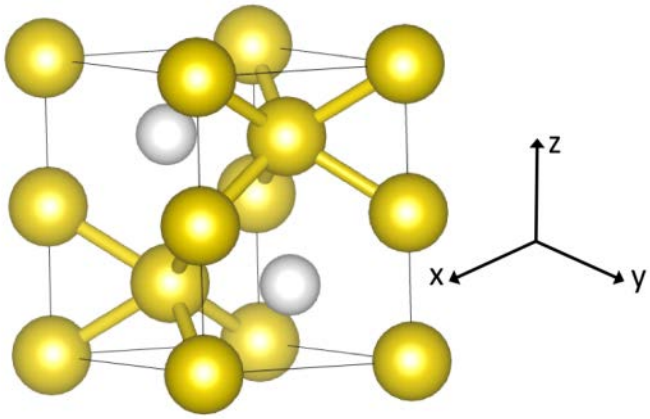


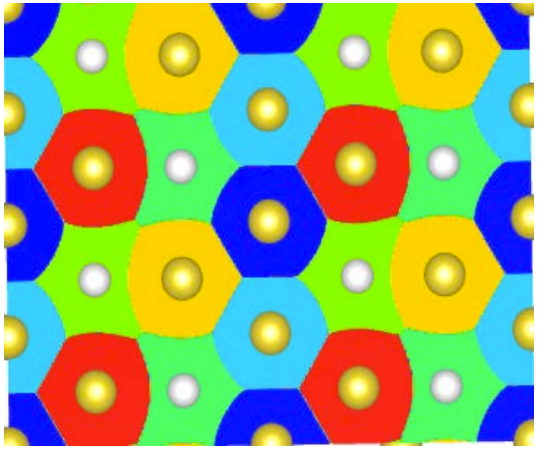
Ni_2In or DHCP

*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.

QTAIM or Bader basins and charges





Charge in electride basin	-0.80	at 100 Gpa
	-1.12	above 200 Gpa
on Cl in NaCl	-0.78	at 1 atm
on O in MgO	-1.74	

A direct comparison with inorganic molecules is posssible

Na_2E E = O, S, Se antifluorite structure at P = 1 atm

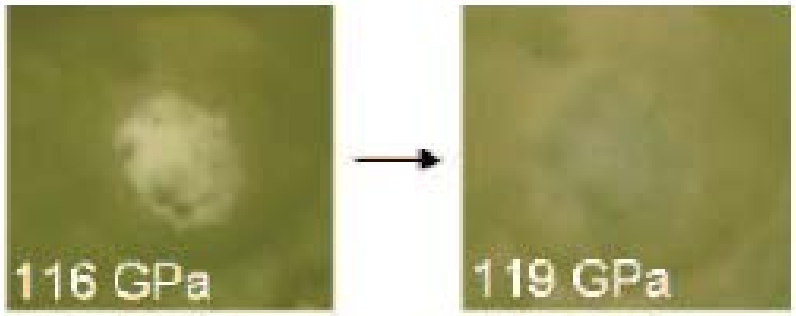
Ni_2In structure at 16 Gpa, (Syassen et al)

	Bader Charge of anion or ISQ (a.u.)	Na^+ volume Å^3	Anion or ISQ volume Å^3
Na HPE 300 GPa	-1.12	4.86	3.58
Na_2S 16 GPa	-1.44	6.32	19.72
Na_2S 300 GPa	-1.38	4.45	12.64
Na_2Se 300 GPa	-1.32	4.52	14.15

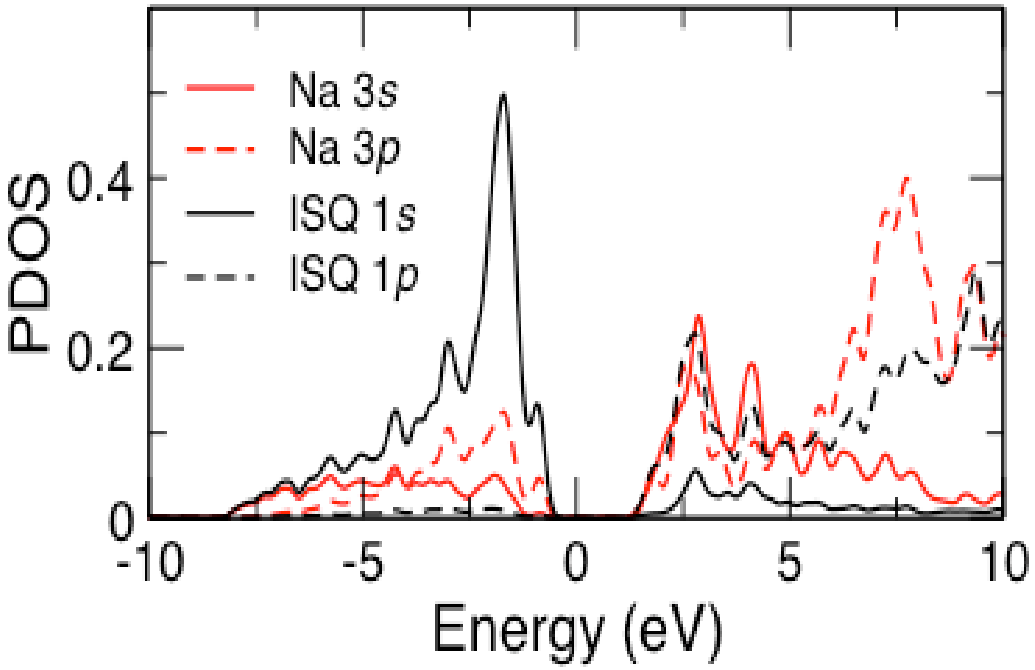
ISQ is much smaller than an S^{2-}; it's about the size of an Na^+

(similar findings by Dong, Oganov, Goncharov et al in Na_2He)

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

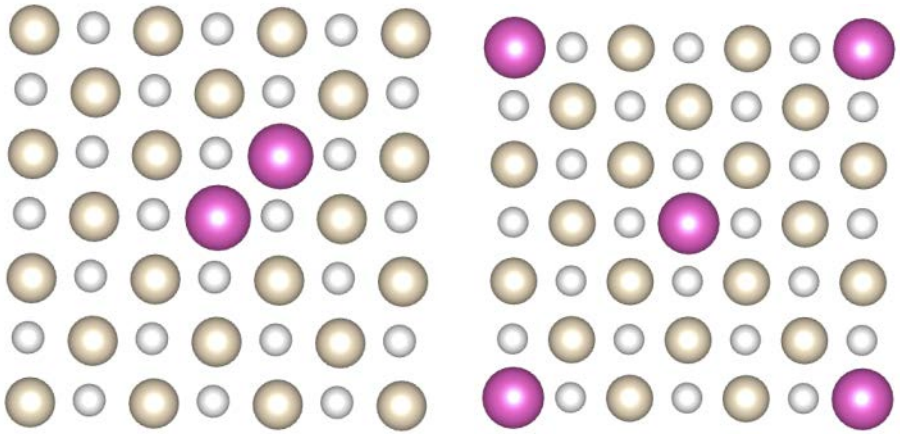


Lazicki, A.; Goncharov, A. F.; Struzhkin, V. V.; Cohen, R. E.; Liu, Z.; Gregoryanz, E.; Guillaume, C.; Mao, H. K.; Hemley, R. J. Anomalous Optical and Electronic Properties of Dense Sodium. *Proc. Nat. Acad. Sci. U.S.A.* **2009**, *106*, 6525-6528

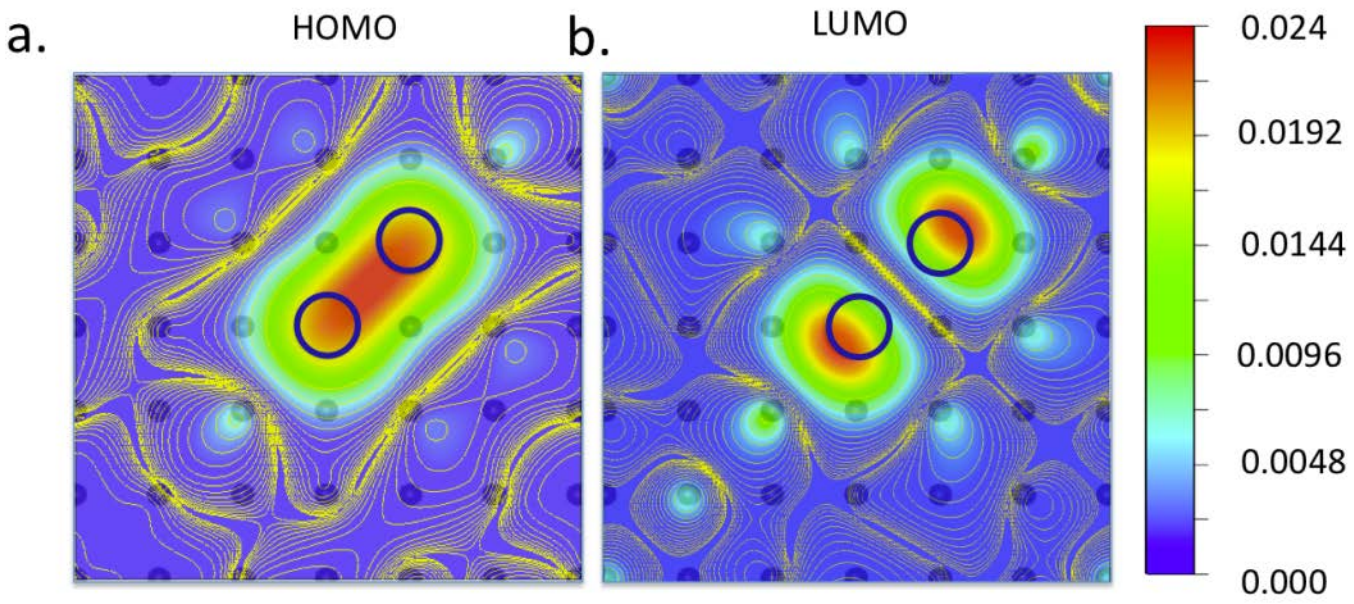


The projected density of states of HPE Na at 300 GPa. Conduction band is ISQ 1p!

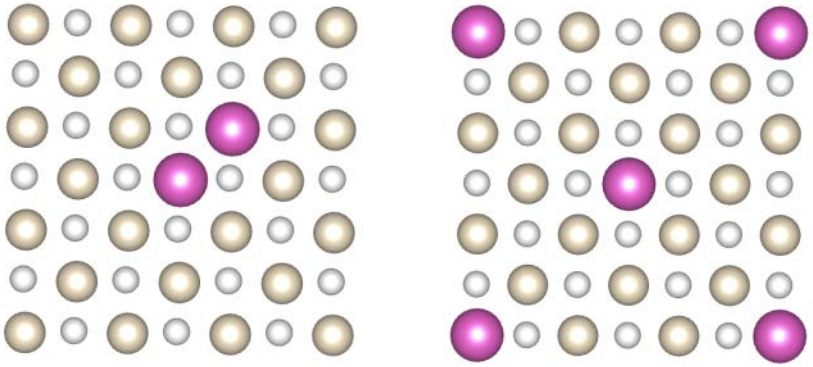
Chemical bonds between ISQs



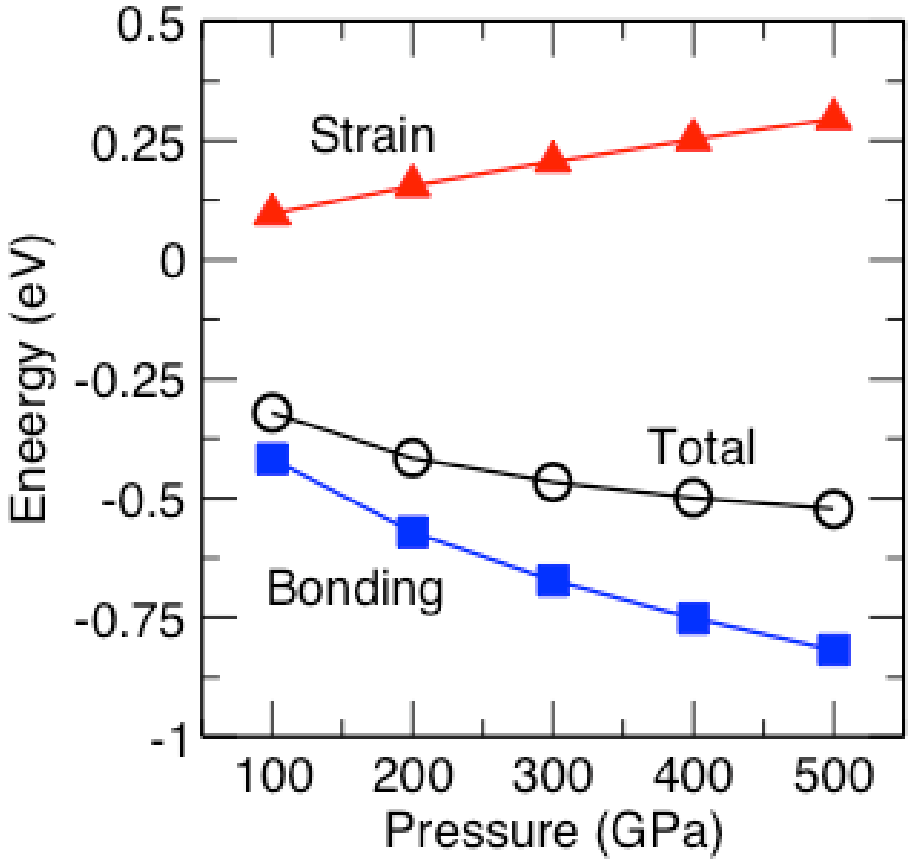
Pressure	E-E (Å)	E……E (Å)
100 GPa	1.70	5.10
500	1.39	4.17

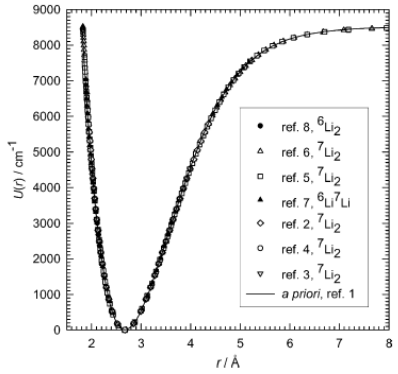


The calculated density of (in unit of electrons/bohr^3) the a) HOMO and b) LUMO of an E-E quasimolecule in the He lattice model, at a minimal ISQ separation of 1.70 Å, at 100 GPa. Small grey spheres represent the position of He atoms in the lattice,



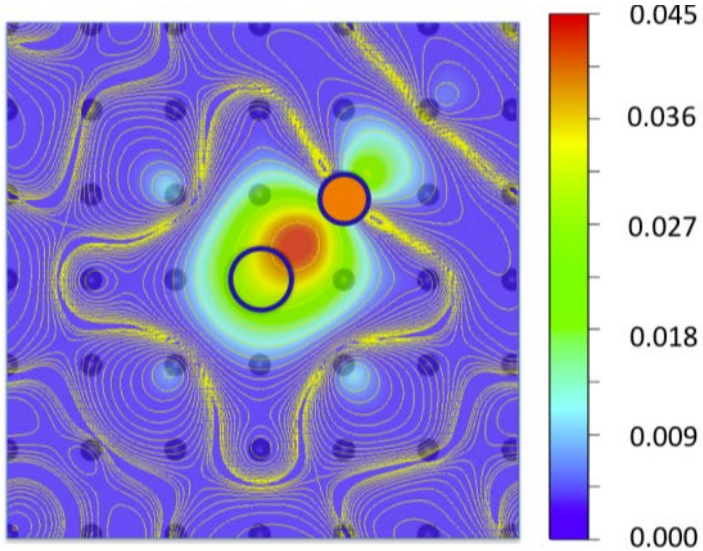
Pressure	E-E (Å)	E……E (Å)
100 GPa	1.70	5.10
500	1.39	4.17





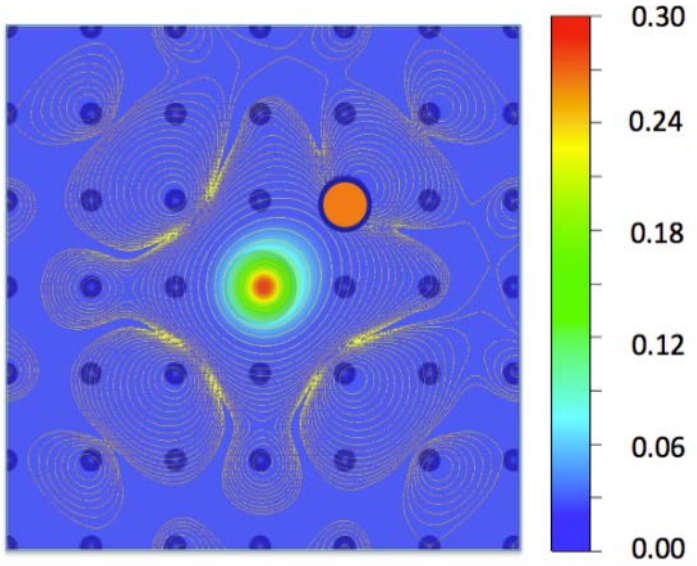
Li_2 A.A. Zavitsas

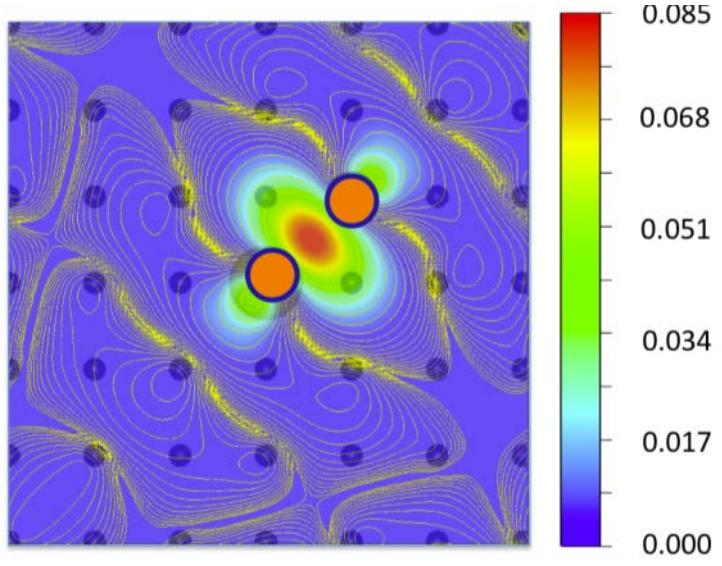
E-Li



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.

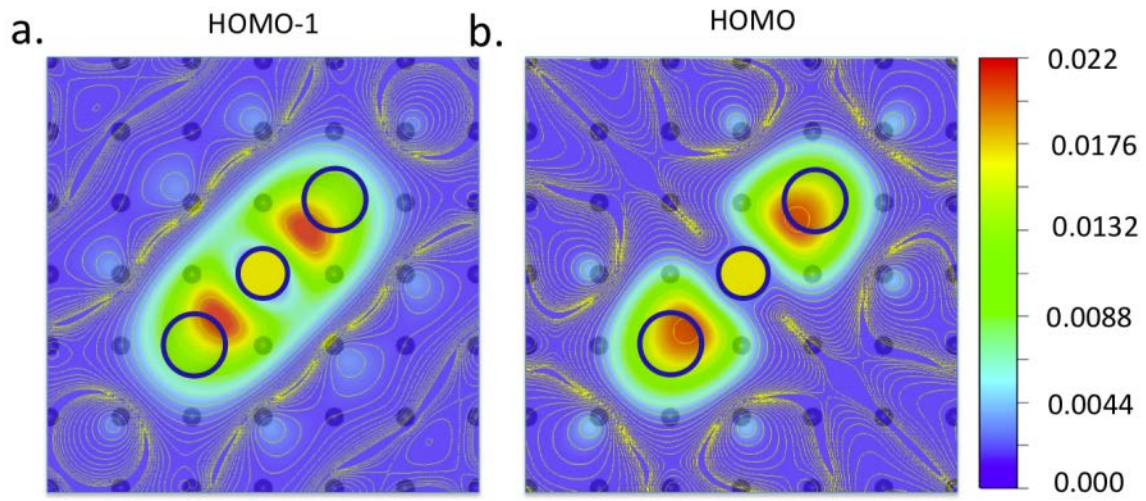
H-Li

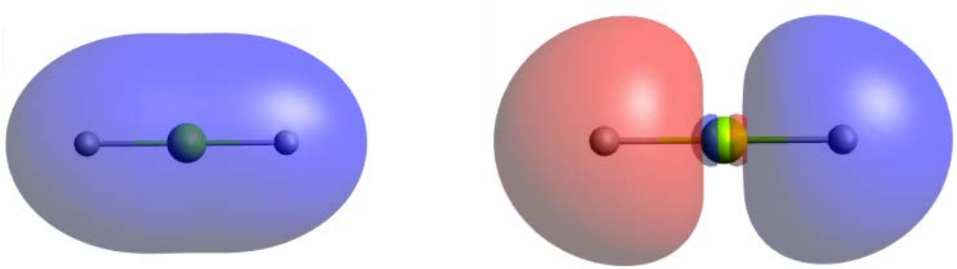




Li-Li

a) Li-H, and b) Li_2 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.



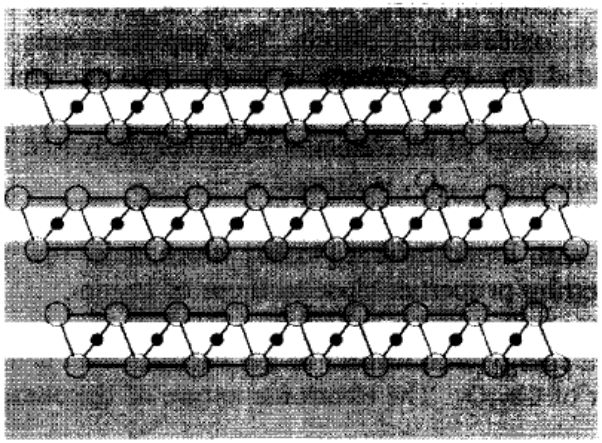


H — Mg — H

Metallic Electrides

at 1atm

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



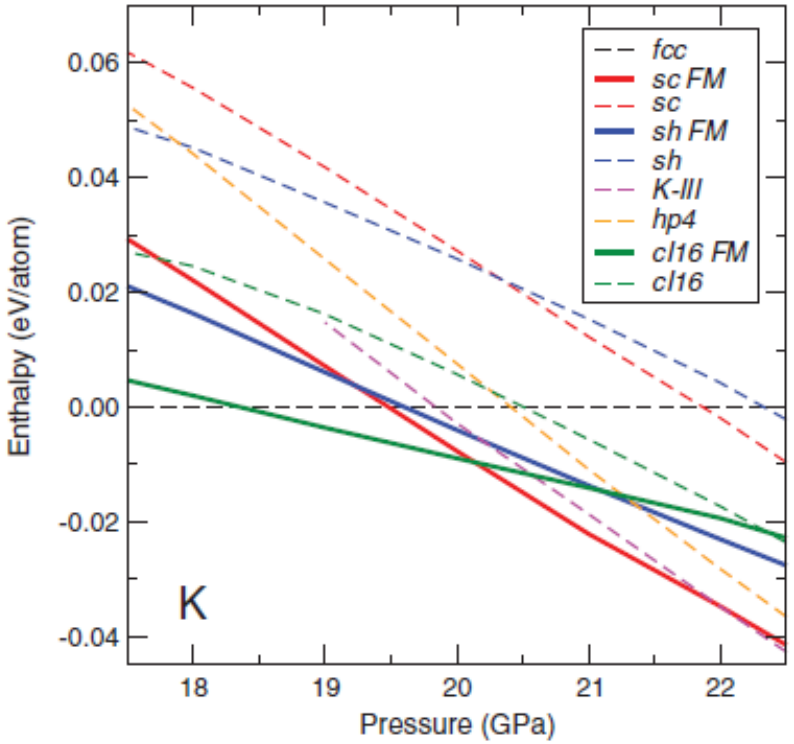
(c)

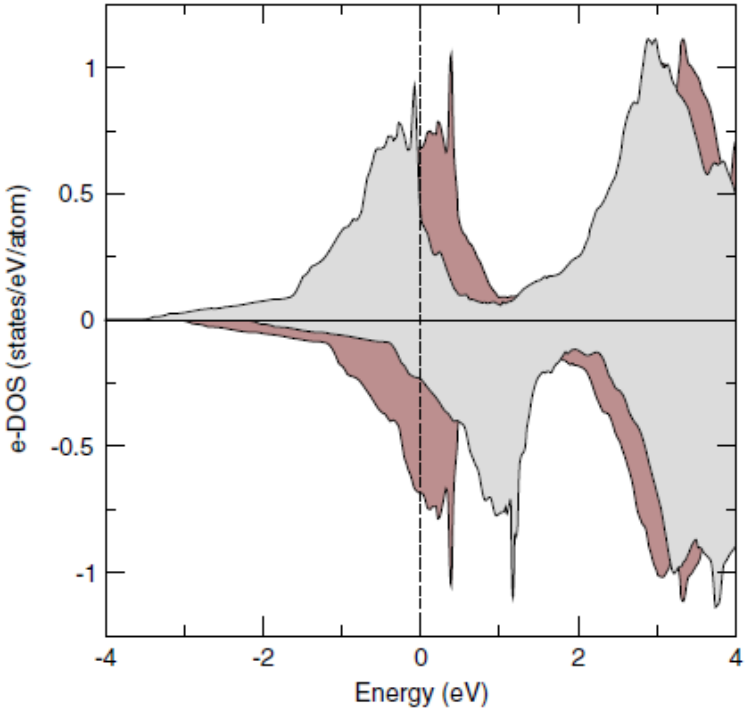
Ba_2N

Fig. 14. Visualization of the real space electronic nature of selected suboxides and subnitrides. The shaded asreas indicate the regions of confinement of the conduction electrons. (a) $Cs_{11}O_3$ shown as a void metal, (b) Na_5Ba_3N representing an atomically drilled metal and (c) Ba_2N shown as a 2D-metal.

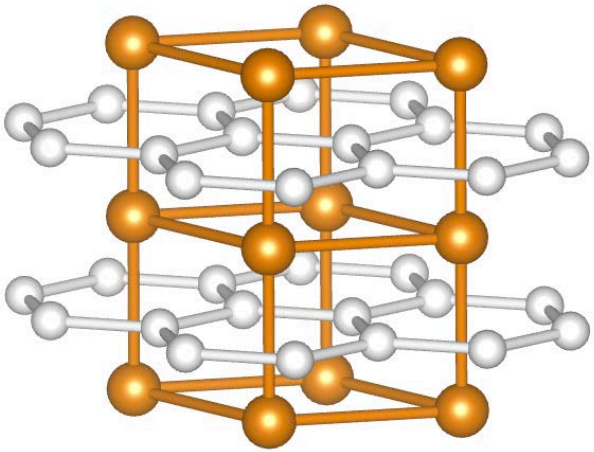
Lee, K.; Kim, S. W.; Toda, Y.; Matsuishi, S.; Hosono, H. Dicalcium Nitride As a Two-Dimensional Electride with an Anionic Electron Layer. *Nature* **2013**, *494*, 336-340.

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

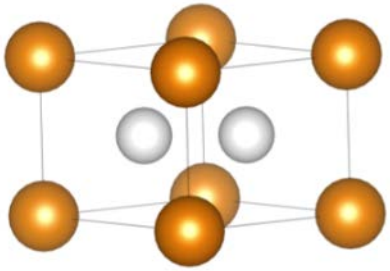




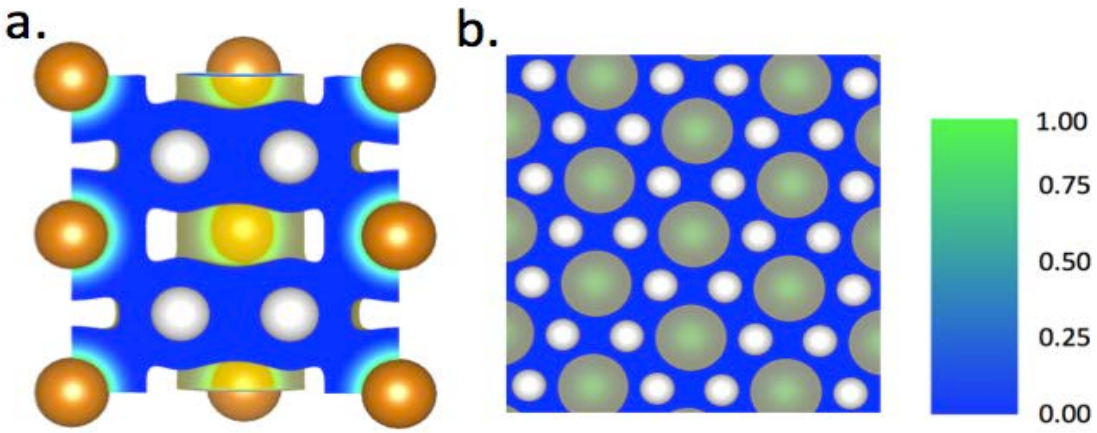
Li, P. F.; Gao, G. Y.; Wang, Y. C.; Ma, Y. M. Crystal Structures and Exotic Behavior of Magnesium under Pressure. *J. Phys. Chem. C* 2010, *114*, 21745-21749.



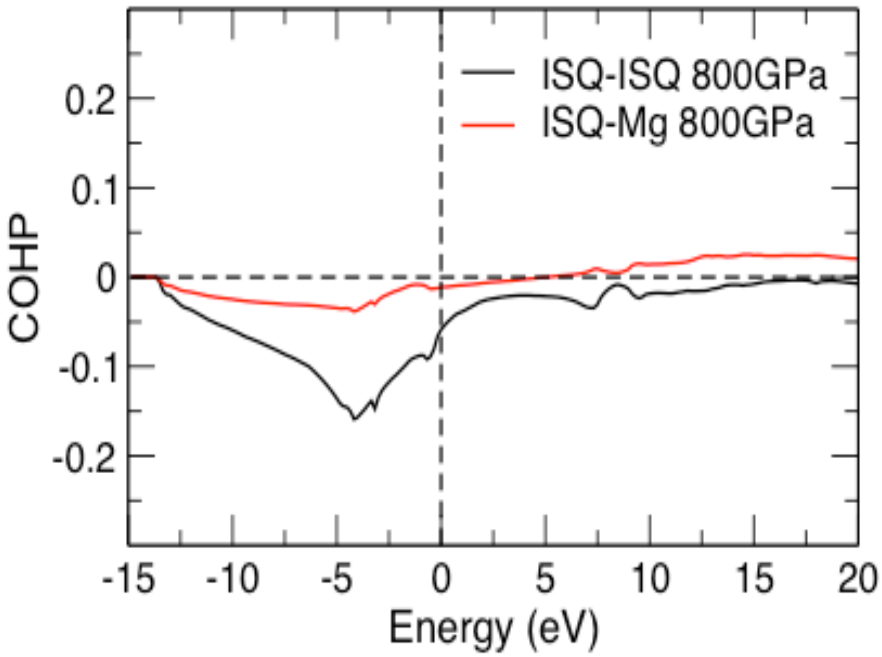
800 GPa, MgB_2 structure



ISQ charge -0.72 (Cl in NaCl -0.78)



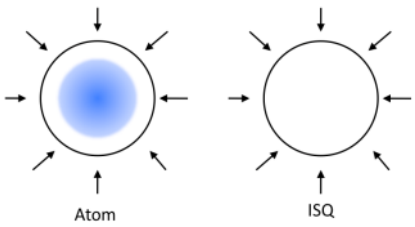
Crystal Orbital Hamiltonian Population analysis of bonding

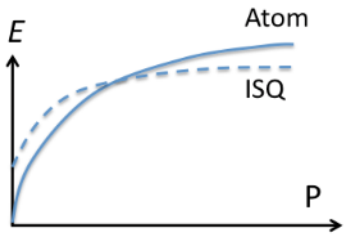


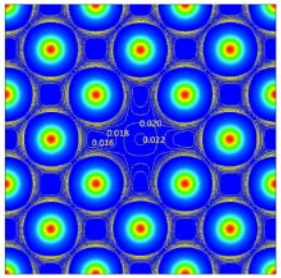
	Integrated COHP
Mg-Mg in HPE	small
Mg-ISQ	-0.32
ISQ-ISQ	-1.17
Diamond CC	-6.52 eV/CC
NaCl	-0.13 eV/NaCl
Metallic Fe	-1.65
Cu-Cu in CuZn	-0.40

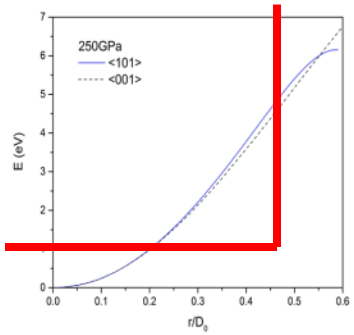
The bonding in the Mg HPE looks like that in an intermetallic compound

ISQ Interstitial Quasi-Atom









1s < 1p <1d ~ 2s

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

#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.

#3 (effect of d orbitals, slopes of different ℓ level with P): 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.

ISQs act as anions, occupying little volume, i.e., high electron density.

ISQs can act as atoms, forming bonds with each other and with certain atoms. And then they can form metallic arrays.

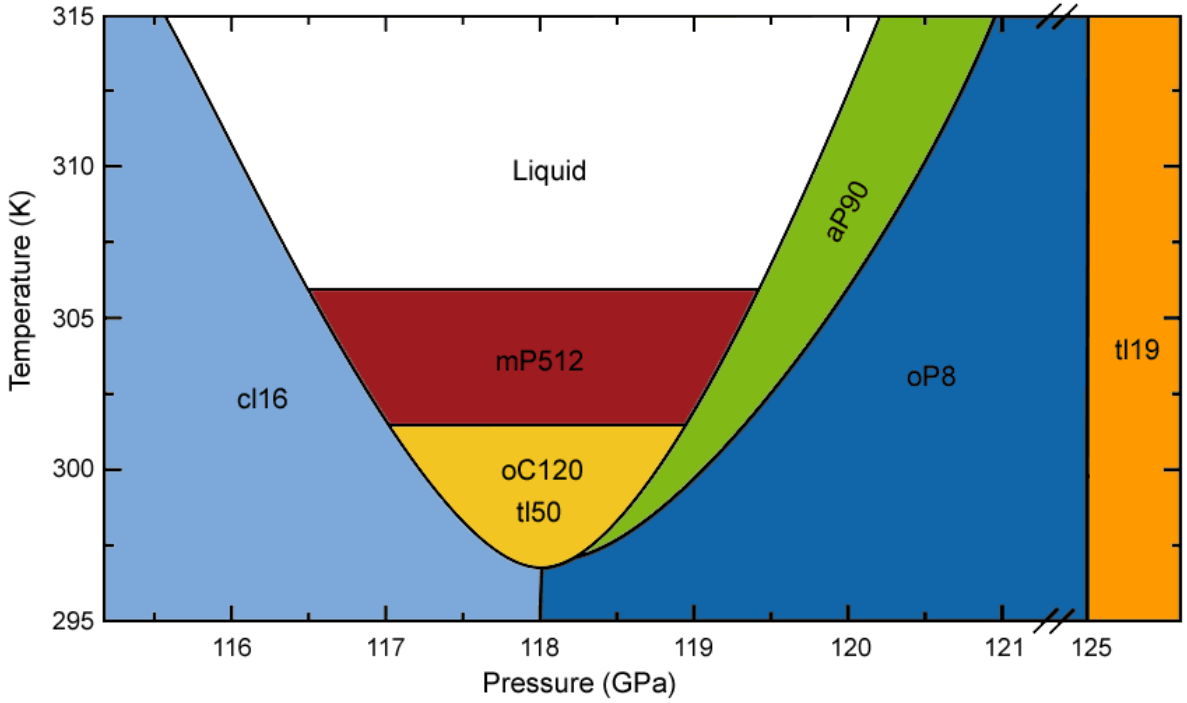
High Pressure Electrides: A Predictive Chemical and Physical Theory

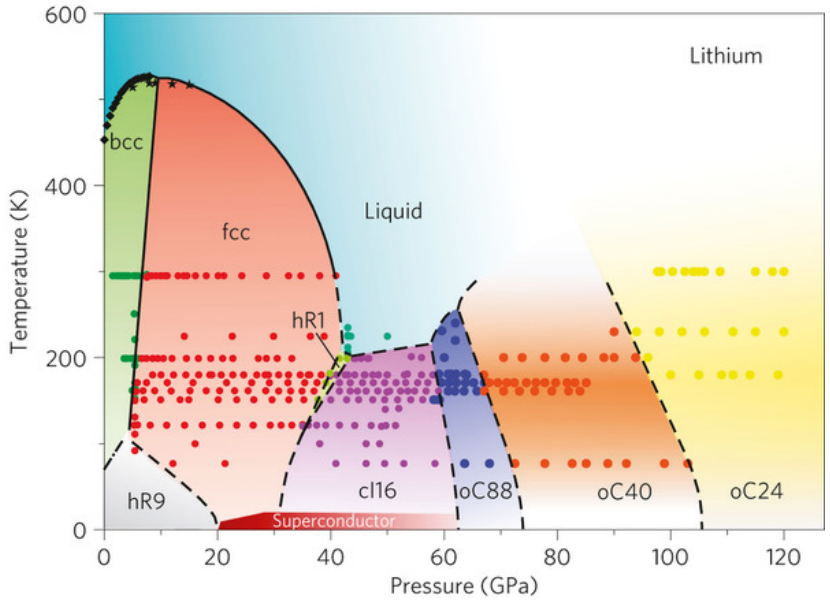
Mao-sheng Miao and Roald Hoffmann

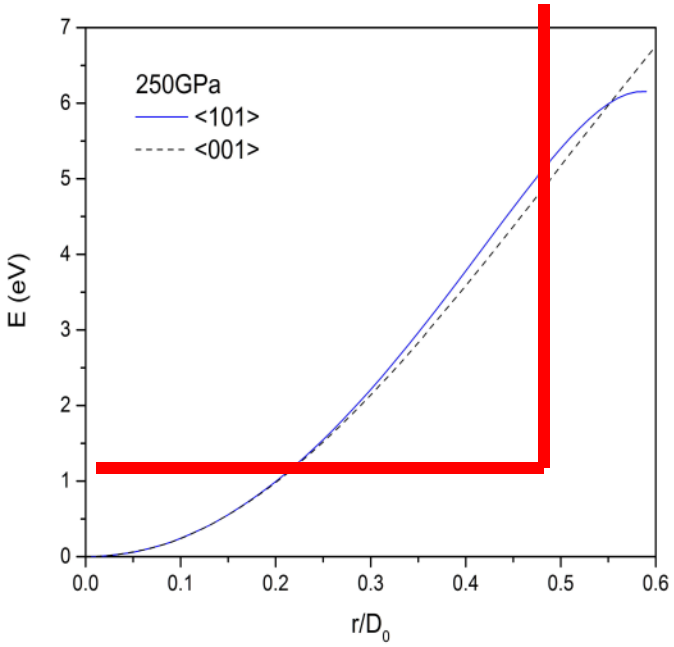
Beijing Computational Science Research Center, Beijing 10084, P. R. China and Department of Physics, California State University Northridge, CA 91330, USA
Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

Accts. Chem. Res. 2014, 47, 1311−1317
and to be published

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).

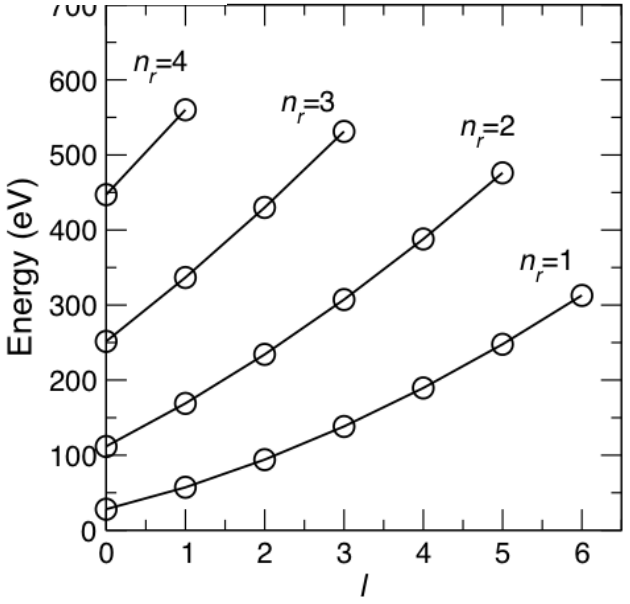

315
310
305
300
295
Temperature (K)
116
117
118
119
120
121
125
Pressure (GPa)
Liquid
aP90
mP512
cI16
oP8
tI19
oC120
tI50


600
400
200
0
Temperature (K)
0
20
40
60
80
100
120
Pressure (GPa)
Lithium
bcc
fcc
Liquid
hR1
hR9
cI16
oC88
oC40
oC24
Superconductor



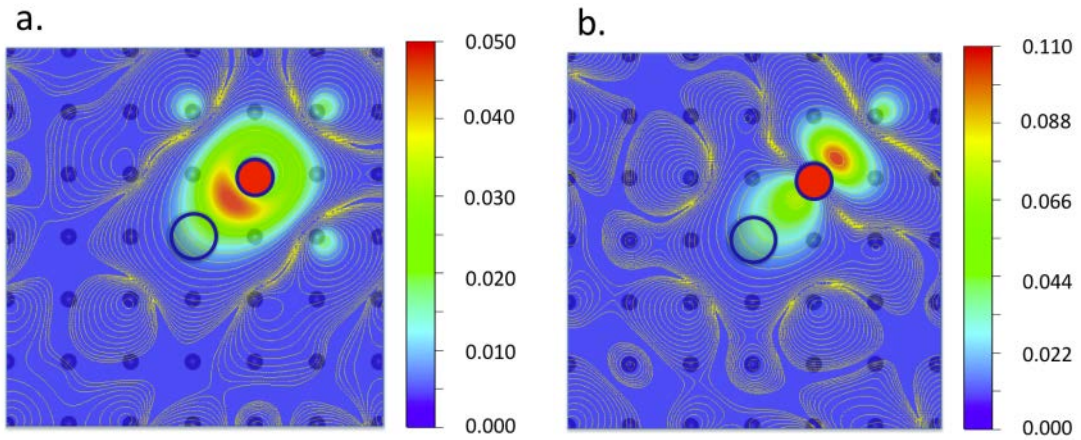
Energy levels of an electron in spherical container for R= 1.16 Å , m=m_e.

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



HOMO LUMO

E-Be



E-B