Activating inner-shell electrons and idle orbitals by high pressure

Maosheng Miao[a,b +]
[a] *Department of Chemistry and Biochemistry, California State University Northridge*
[b] *Beijing Computational Science Research Center, Beijing, China*

The chemistry at ambient condition has implicit boundaries rooted in the atomic shell struc- ture: the inner-shell electrons and the unoccupied outer-shell orbitals do not involve as major component in chemical reactions and in chemical bonds. The chemical properties of atoms are determined by the electrons in the outermost shell; hence, these electrons are called valence electrons. These general rules govern our understanding of chemical structures and reactions.

Using first principles calculations, we demonstrate that under high pressure, the above doctrines can be broken. We show that both the inner shell electrons and the outer shell empty orbitals of Cs and other elements can involve in chemical reactions. In the presence of fluorine and under pressure, the formation of CsF_n ($n > 1$) compounds containing neutral or ionic molecules is predicted.[1] Their geometry and bonding resemble that of isoelectronic XeF_n molecules, showing a caesium atom that behaves chemically like a p-block element under these conditions. Furthermore, we find that under high pressure Hg in Hg-F compounds transfers charge from the d orbitals to the F, thus behaving as a transition metal. Oxidizing Hg to + 4 and + 3 yielded the thermodynamically stable compounds HgF_4 and HgF_3.[2] The former consists of HgF_4 planar molecules. HgF_3 is metallic and ferromagnetic, with a large gap between its partially occupied and unoccupied bands under high pressure.

Electrides are materials in which some valence electrons are separated from all atoms and occupy interstitial regions, effectively forming anions with no centering nuclei nor core electrons. Recently, it is found that, under high pressure, alkali metals such as Li and Na become semiconducting or insulating. As they do so, they adopt structures containing sites that accommodate electrons, leading to the formation of high-pressure electrides (HPE). Similar phenomena have also been predicted for Mg, Al and several other materials. The driving force for HPE formation may be attributed to the lack of core electrons in the interstitial sites, which causes the energies of the corresponding quantized orbitals to increase less significantly with pressure than normal atomic orbitals.[4] These empty sites enclosed by surrounding atoms have been termed interstitial quasiatoms (ISQ); they may show some of the chemical features of atoms, including the potential of forming covalent bonds. Here we argue that some calculated ISQs in the high-pressure semiconducting Li phase (oC40, *Aba*2) actually form covalently bonded pairs.[5] We suggest such quasimolecules may be found in other systems at high pressures as well.

1. M. S. Miao, ***Nature Chemistry***, 5, 846 (2013).
2. J. Botana, X. Wang, C. Hou, D. Yan, H. Lin, Y. Ma and M. S. Miao, ***Angew. Chemie*** 54, 9280-9283 (2015).
3. M. S. Miao, X. L. Wang, J. Brgoch, . Spera, M. G. Jackson, G. Kresse, and H. Q. Lin, ***J. Am. Chem. Soc.*** 137, 14122 (2015)
4. M. S. Miao and R. Hoffmann, ***Accounts of Chemical Research,*** 47, 1311 (2014).
5. M. S. Miao, R. Hoffmann, J. Botana, I. I. Naumov and R. J. Hemley, ***Angew. Chemie*** 56, 972 (2017).