Chemical Bonding across the Periodic Table at High and Ambient Pressures

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Abstract:
Part of our research is devoted to the properties of hydrogen-rich materials, especially under high pressure. In this area, we have built on previous work at the Cornell NanoScale Facility to further our understanding of the W-H phase diagram [1]. We also searched for new stable ice phases at very high pressures [2], and contributed to a deeper understanding of the physics and chemistry involved in some of the high-pressure phases of pure hydrogen [3]. We also studied the ternary phase diagram of the light elements Li-Be-B, which involved comprehensive studies of the binary phases Be-B and Li-B as well [4].

Summary of Research:
1. Molecular Models for Tungsten Hydrides. At atmospheric pressure, some tungsten hydrides exist as discrete molecular complexes in low temperature matrices, but are very reactive and cannot be isolated in bulk at room temperature. Under pressure, one observes WH in experiment at room T, and calculations indicate several other stoichiometries are stable, all extended and not molecular. This work aimed at constructing a bridge between discrete molecules and the pressurized extended structures, with the emblematic example of WH₆. The equilibrium structure, known as a distorted trigonal prismatic molecule, is likely to be a good acceptor. In numerical experiments, discrete WH₆ molecular complexes are allowed to interact with each other at T = 0K and P = 1 atm. They spontaneously rearrange to form 1D-chains, with the W centers adopting a tricapped trigonal prismatic environment. The electronic structure of these chains is examined and related to that of the monomer and extended solids [1].

2. High Pressure Ice Phases. From computational evolutionary structure searches, we find a sequence of new stable and meta-stable structures for the ground state of ice in the 10…50 Mbar regime, in the static approximation [2]. We find a new Pmc2₁ phase to be stable at P = 9.3 Mbar, followed by a transition to a high-coordinated P2₁ structure at P = 13 Mbar. These new structures are insulating — chemistry burns a deep and (with pressure increase) lasting hole in the density of states near the highest occupied electronic levels of what might be component metallic lattices. Metallization of ice in our calculations occurs only near P = 48 Mbar, where the intrinsically metallic C2/m phase becomes most stable. We analyze carefully the geometrical changes in the calculated structures, especially the buckling at the H in O-H-O motifs. In the Mbar pressure regime, zero-point energies much larger than typical enthalpy differences suggest possible melting of the H sublattice, or even the entire crystal.
3. Understanding Hydrogen Under Pressure. Dense hydrogen, despite its apparent simplicity, is a challenging system for experimentalists and theoreticians alike. But understanding this fundamental system remains an important area of study, as dense hydrogen comprises a large fraction of the universe in the form of stars and planets. Results of both experimental and theoretical studies of dense hydrogen reveal a surprising richness of behavior in this complex and intriguing system. Our results, published in a series of four papers [3], present a fresh look at molecular hydrogen under pressure and its transition from a molecular to a monatomic, metallic state. Using a numerical laboratory of the best static structures calculated for hydrogen, we find in it an approach to metallization that preserves some features of diatomic molecules as well as opposing effects influencing distances in the compressed solid — a physical one of containment, and an orbital/chemical one of essentially donor-acceptor bonding between hydrogen molecules (making a connection to the side-on bonded dihydrogen organometallics). We also explore a model with lovely symmetry that makes a single-parameter transition between a molecular solid and a highly compressed monatomic one.

4. Ternary Light Element Compounds. Beginning an in-depth analysis of binaries and ternaries in the Li/Be/B system, we examined the static structures and electronic properties of LiBeB (i.e., 1:1:1) over a range of pressures [4]. This as yet unknown compound is predicted to possess a stable ground state at P = 1 atm and some higher pressures. As the pressure rises, LiBeB goes through a diverse series of structures, beginning with metallic structures which feature chains and layers of atoms, progressing to structures built on “colorings” of the Laves phases, and containing helical arrangements of boron atoms, on to high pressure phases that are ternary variants of a bcc lattice. We find some curious features in the LiBeB structures, these include near-icosahedral coordination, independent of atom type; in a range of pressures a resemblance of the total DOS to that of metallic Be; and also a Dirac surface.

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