Metal insulator transition in molecular hydrogens under high pressure

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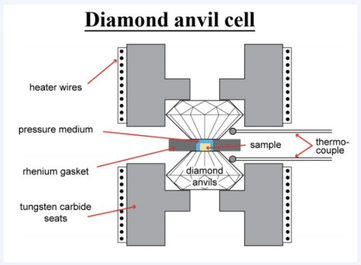
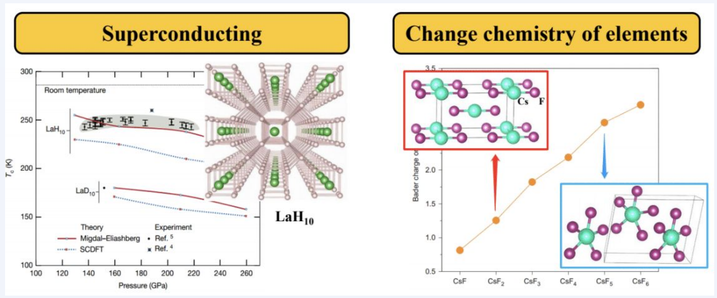
Abstract

At higher pressures, molecular hydrogen breaks apart, forming extended covalent networks that enable electron delocalization. This metallic hydrogen, a longstanding goal in high-pressure physics for achieving high-temperature superconductivity, remains elusive due to numerous technical challenges. Interestingly, a metal-insulator transition may occur at lower pressures in hydrogen molecular crystals, where H_2 molecules retain their molecular characteristics. We studied this phenomenon using first-principles density functional theory (DFT) calculations with semilocal and hybrid functionals, observing changes in electron distribution that drive the transition. Under increased pressure, H_2 bond lengths stretch, pushing electrons into interstitial sites while maintaining structural stability. This process results in a metal-insulator transition (MIT), where molecular hydrogen shifts from an insulating to a metallic phase. Similar to the extended hydrogen networks in the metallic phase, the interstitial electron states enhance electron-phonon interactions, which are key to achieving high-temperature superconductivity.

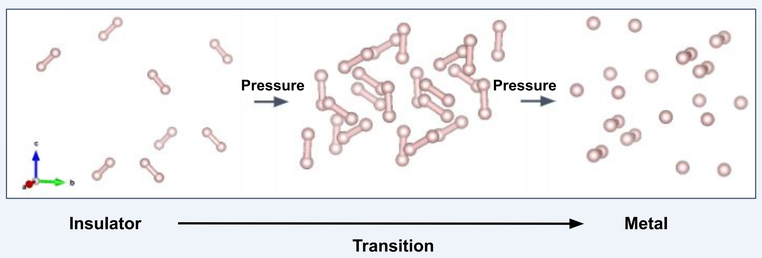
High Pressure Chemistry

- High-pressure chemistry unveils unique material structures and compounds unobservable at standard pressures, leading to discoveries like phase transitions and unusual stoichiometries.
- Advanced computational simulations predict high-pressure behaviors, guiding experimentalists toward promising research avenues and optimizing resource utilization.
- High pressures can induce superconductivity, transform the typical chemistry of elements, and stabilize compounds with distinctive electronic, mechanical, and optical characteristics.





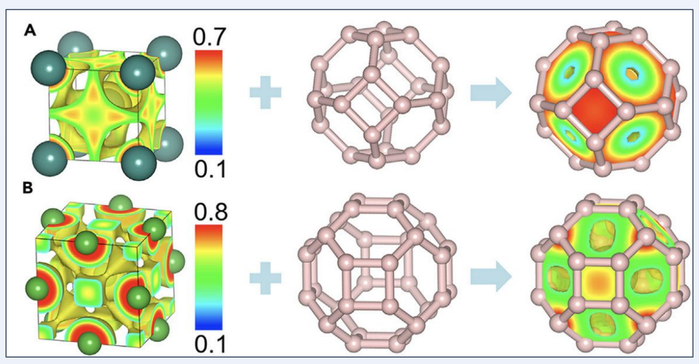
Hydrogen in Superconductivity



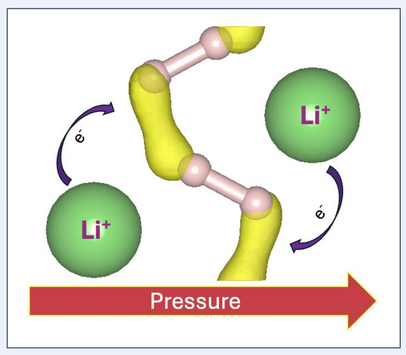
- In 1968, Ashcroft proposed that metallic hydrogen could become a high-temperature superconductor due to its light atomic mass and strong electron-phonon coupling.
- *When high pressure is applied to H_2, and it is observed that the molecular bonds elongate as intermolecular distances decreased.
- At sufficiently high pressures, the elongated H_2 bonds break apart, leading to atomic hydrogen.
- This work aims to explain the underlying mechanisms driving the transition from molecular to atomic hydrogen under high pressure.

Metal Superhydrides

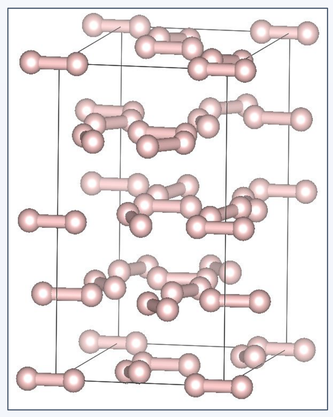
- Metal superhydrides act like metallic hydrogen by using large metal ions to stabilize the hydrogen atom network.
- Atomized hydrogen networks form extended 3D structures under high pressure.
- These networks provide pathways for electron delocalization, facilitating free electron movement and electron-phonon coupling.

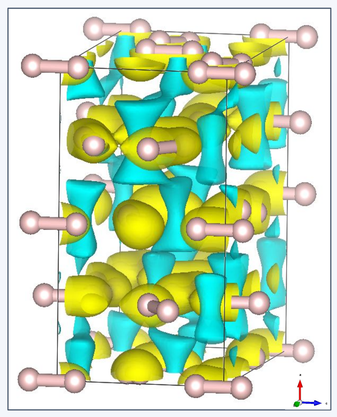


- If the metal insulator transition (MIT) occurs while hydrogen is molecular, this begs the question of molecular superhydrides.*
- Since the molecular H_2 bond doesn't need to be split this means superconductivity is potentially achievable at lower pressures.



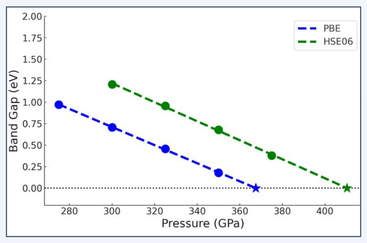
Metal Insulator Transition of Molecular Hydrogen

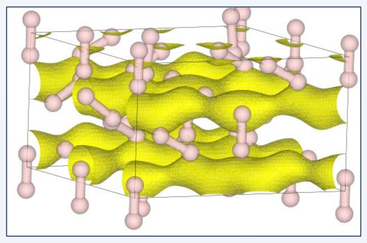


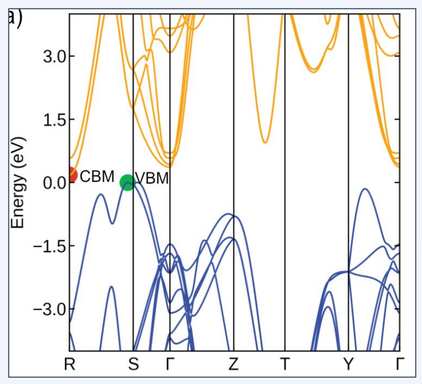


- This delocalization is driven by a combination of increased bond length and compressed atomic distances, which force electrons into interstitial regions.
- Charge density difference between the H_2 lattice and H_2 molecules and wavefunction displays transfer of electrons to interstitial sites.

- The *Ama*2 phases maintains molecular (H_2) covalent bonds.
- As pressure increases, antibonding states in molecular hydrogen phases become progressively lower in energy.
- This leads to the partial occupation of these states at the conduction band minimum, transitioning to a metal.*
- The occupation results in the delocalization of electrons, as they are no longer confined to localized H_2 bonds.



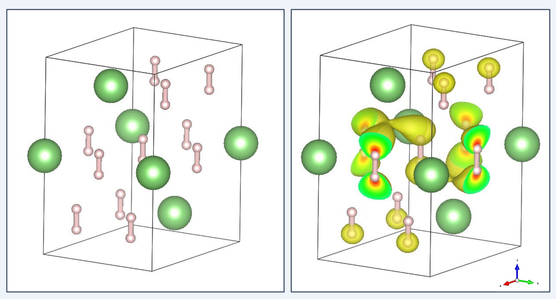


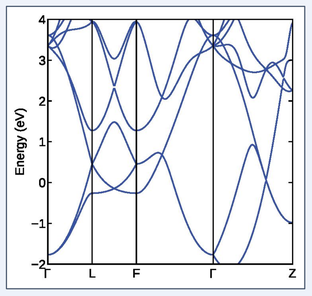


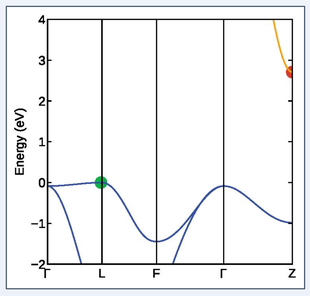
- Use of HSE06 functional accounts for the band gap underestimation issue of PBE, increasing the predicted metallization pressure by almost 75 GPa.
- The closing of the band gap results in the electron delocalization, forming an extended network within the lattice and the onset of metallic behavior necessary for eventual superconductivity.

H_2 Sublattice Doping

- Introducing lithium into the H_2 sublattice facilitates metallization at lower pressures
- Lithium donates electrons that raise the Fermi level and occupy the antibonding (σ*) orbitals of H_2 molecules, destabilizing H–H bonds, reducing the energy gap, and enhancing orbital overlap among neighboring molecules.







- By comparison, the H_2 sublattice (Li_0H_6) is still not metallic at 20 GPa while the 0 GPa relaxed structure of LiH_6 has overlapping bands
- The HOMO of LiH_6 indicates formation of electron interstitial network even when relaxed to ambient pressure due to doping

Conclusions

- Under high pressure, molecular hydrogen transitions from an insulating phase with localized electrons to a metallic phase where electrons delocalize into interstitial sites, forming extended networks that enhance conductivity
- The delocalization of electrons and occupation of lower-energy antibonding states in these high-pressure phases play a critical role in enabling strong electron-phonon coupling, leading to the possibility of high-temperature superconductivity in hydrogen-rich systems

Acknowledgements

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