Band gap closure under pressure in phase III and phase IV of molecular hydrogen by Quantum Monte Carlo.

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We investigate the closure of the fundamental band-gap under pressure in the phases III and IV of crystalline molecular hydrogen beyond 250GPa. We apply Grand-Canonical Reptation Quantum Monte Carlo (GC-RMC) with twisted-boundary conditions to analyze energies of systems of N_p protons and a number of electrons in the range $[N_p\text{-}n;N_p+n]$ with n=2,4,6. Finite temperature effects are considered by averaging over nuclear configurations obtained by Coupled Electron-Ion simulations at finite temperature [1]. Nuclear quantum effects are considered by representing nuclei by Path Integral.

We investigate two candidate structures of Phase III, namely C2/c and Cmca12, and the structure Pc48 candidate for phase IV [1]. For ideal crystalline structures (classical nuclei in the perfect crystal configuration) the band gap closes above 400GPa, slightly earlier for the Cmca12 than for the C2/c structure. Nuclear quantum and thermal effects are found to reduce considerably the amplitude of the gap, shifting the closing pressure between 350GPa and 400GPa. By a directional analysis of our data we find a strong directional character of the gap amplitude which suggests the presence of an indirect gap and the semimetallic character of the system at the closing pressure and at pressure just above. This scenario is in agreement with predictions based on Density Functional Theory [1] and with recent experiments [2].

REFERENCES

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