New Method for Computing Band Gaps from Grand Canonical Quantum Monte Carlo Calculations Applied to Solid Hydrogen.

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Text should be in Times New Roman, 10 points. Please do not change margin size. Each paragraph should be indented. References should appears as apex like this.[1] Reference format as the example below. Graphics and Tables can be embedded in the text We propose a purely variational method for computing band gaps within quantum Monte Carlo (QMC) simulation. Based on grand canonical reptation quantum Monte Carlo (GC-RQMC) with twisted boundary conditions, we analyze energies of systems of N_p protons varying the number of electrons, N_e, from N_p-Δ_N to N_p+Δ_N. Total neutral magnetization is assured by adding/subtracting always even number of electrons whereas odd numbers probe spin excitations. Grand canonical analysis can be done as a post processing converting the dependency on the number of electrons N_e in favour of the chemical potential μ. Different twists are used to correct all single particle size effects, two-particle size effects are corrected by analyzing the structure factor $S(k,\mu)$ \cite{SizeEff}.

We apply this new technique to compute the band gap of solid molecular hydrogen beyond 250 GPa. We investigate two candidate structures of phase III: C2/c and Cmca12 \cite{Struct}. For these crystalline structures at zero temperature the band gap closes above 400 GPa, for the Cmca12 at slightly lower pressure than for the C2/c. From the variation of the momentum distribution $n(k,\mu)$ with respect to the chemical potential, we argue that the band gap is indirect. These results are in reasonable agreement with predictions based on QMC corrected Density Functional Theory (DFT) \cite{Azadi}. Our purely QMC based method allows us to gain more understanding and better insight from a many-body prospective without relying on a specific DFT functional. Furthermore, our scheme can be straightforwardly applied to more general situations including thermal and zero point motion of protons beyond the harmonic approximation.

1. M. Holzmann, R. C. Clay, M. A. Morales, N. M. Tubman, D. M. Ceperley and C. Pierleoni, *Phys. Rev. B* **2016,** 94, 035126.

2. G. Rillo, M. A. Morales, D. M. Ceperley, and C. Pierleoni, *J. Chem. Phys.* **2018 ,** 148, 102314.

3. S. Azadi, N. D. Drummond and W. M. C. Foulkes, *Phys. Rev. B* **2016** 95, 035142**.**