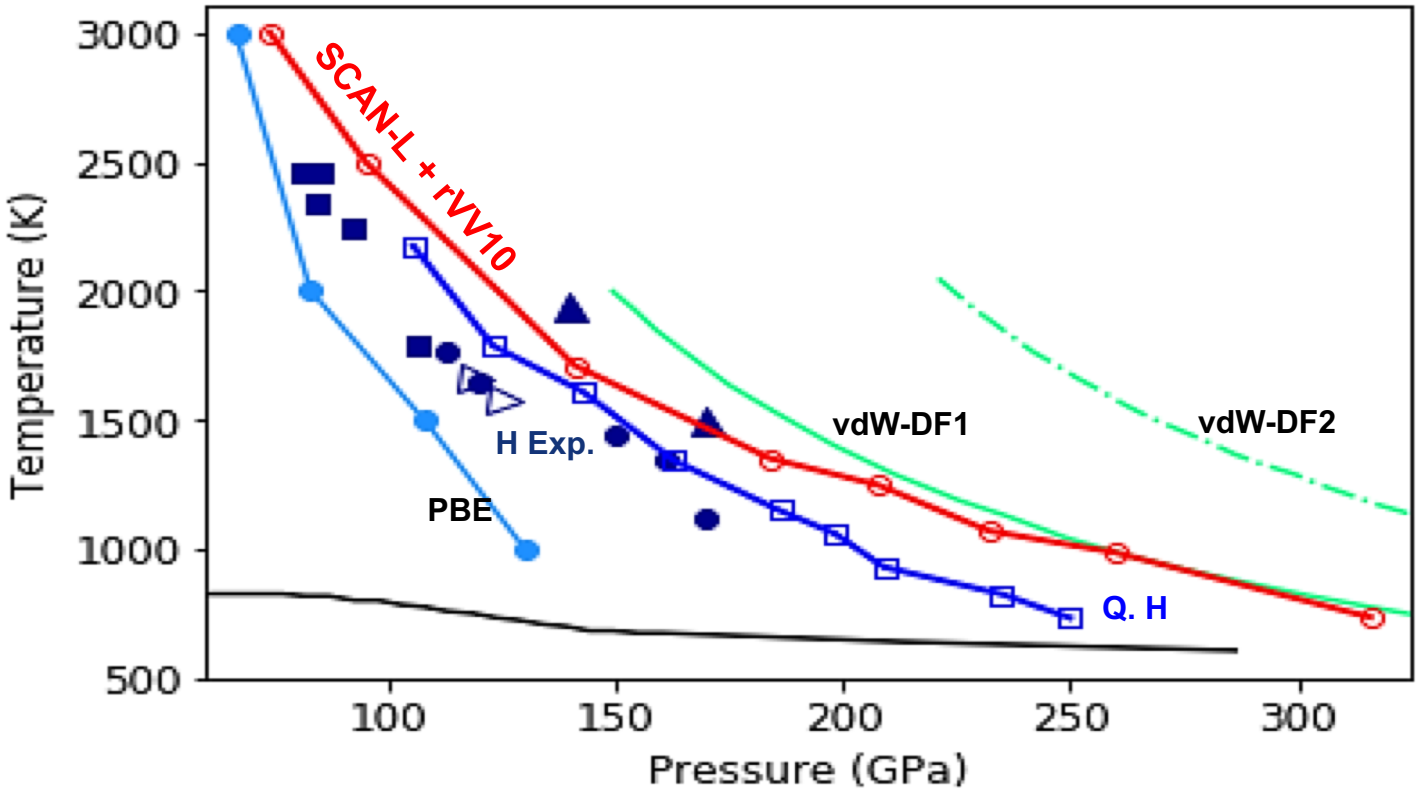
# First principles investigation of the insulator-metal transition in liquid hydrogen with a recently developed deorbitalized meta-GGA exchange-correlation functional

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Laboratory for Laser Energetics

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Division of Plasma Physics
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## Summary

**The insulator-metal transition (IMT) of fluid hydrogen has been determined through *ab initio* quantum molecular dynamic simulations with a metaGGA level exchange correlation (XC) functional.**

- **The resulting IMT is in better agreement with experimental measurements as compared to previous density functional theory studies.**
- **Analysis of the optical and structural properties of the system all show abrupt changes that coincide with the onset of a minimum metallic dc conductivity of 2000 S/cm.**
- **The inclusion of nuclear quantum effects significantly accelerates the dissociation of molecular hydrogen prior to the metallic transition resulting is a significant shift in the IMT boundary.**

**In total, these results support the idea of a metallic transition caused by an abrupt band gap closure directly associated with the dissociation of molecular insulating hydrogen into atomic metallic hydrogen.**

# Collaborators and Funding

**Valentin Karasiev**
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**Daniel Mejia-Rodriguez**
University of Florida, Quantum Theory Project

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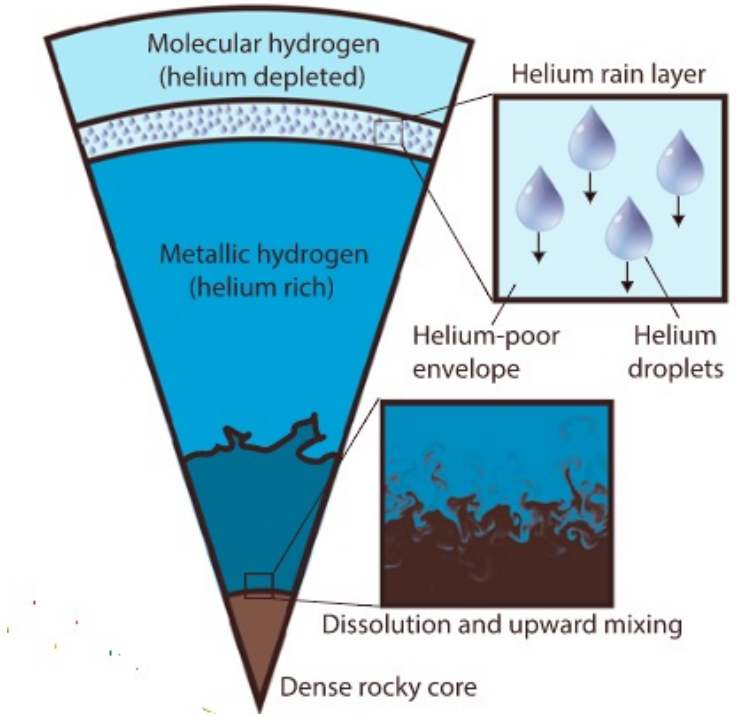
- DMR acknowledges support by U.S. Dept. of Energy grant DE-SC 0002139.

# An accurate equation of state (EOS) of warm dense fluid hydrogen is of fundamental importance in a wide range of research from planetary science to inertial confinement fusion (ICF).

- **The insulator to metal transition (IMT) of hydrogen is believed to be the catalyst for H-He demixing within Jovian like planets.**
- **Additionally the metallization of H is an important feature in understanding the dynamo processes that occur in such planets.**
- **Furthermore, an accurate EOS that captures correctly the IMT is key in the design and development of capsules used in ICF research.**





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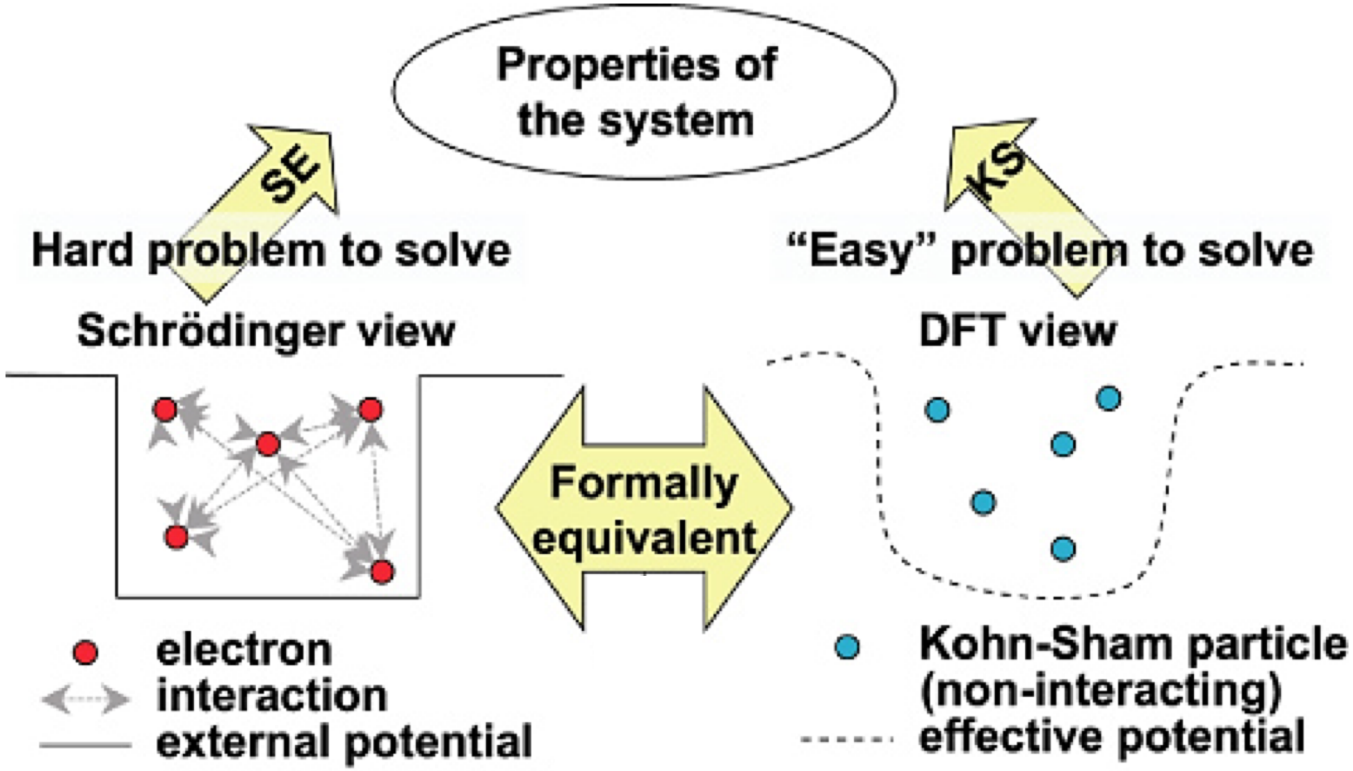
Hu *et al*, Phys Plasmas, 22, 056304 (2015).
S.M. Wahl *et al*, Geophys Res Lett, 44, 4649 (2017).

# *Ab initio* quantum molecular dynamic simulations are performed within the frame-work of density functional theory to determine the IMT of fluid hydrogen.

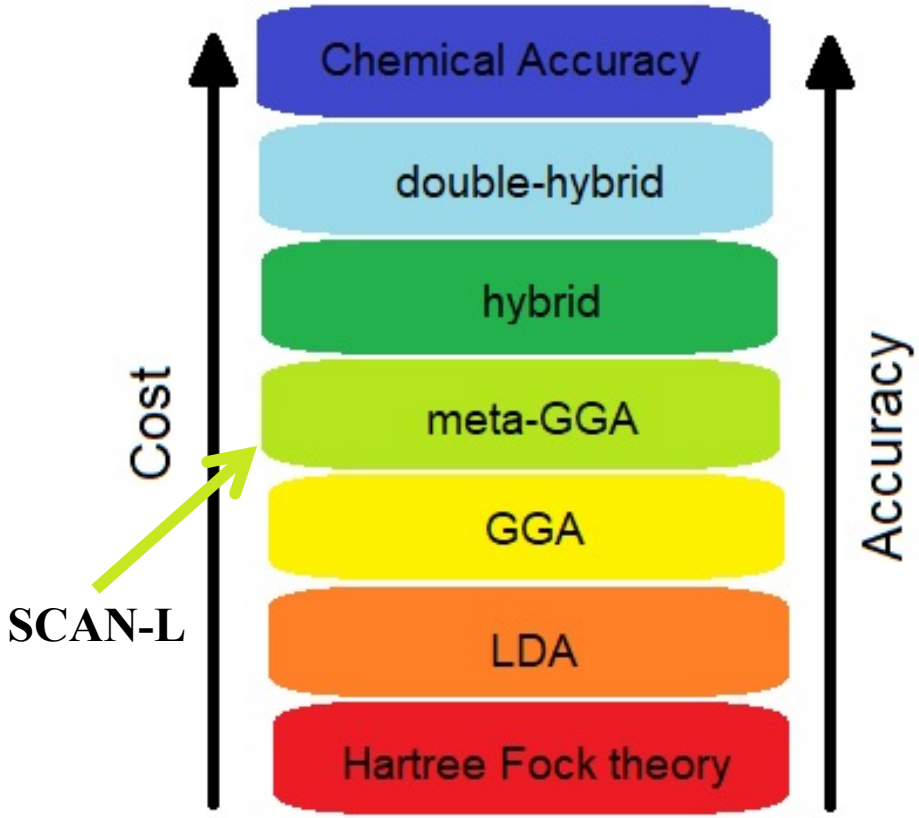
- **Ions:**
  - **Case 1: Treated classically within the Born-Oppenheimer Molecular dynamics (BOMD).**
    - **VASP, 256 atom system**
  - **Case 2: Treated quantum mechanically within Path Integral Molecular dynamics (PIMD).**
    - **QE, 256 atom system**
- **Electrons:**
  - **Always treated quantum mechanically within Mermin-Kohn-Sham DFT.**




D. Marx, M Parrinello, J Chem Phys, 104 (1996).
W. Khon, L.J. Sham, Phys Rev, 140, A1133 (1965).

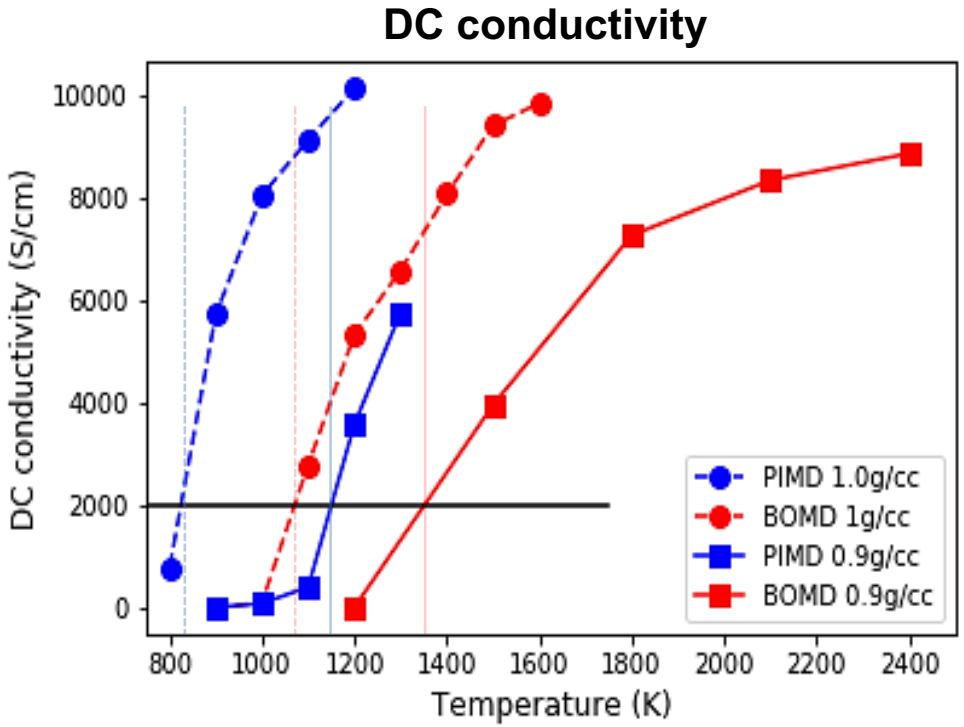
# The exchange-correlation (XC) energy of the electrons is calculated with the deorbitalized version of the MetaGGA SCAN (SCAN-L) with the non-local correlation correction rVV10.

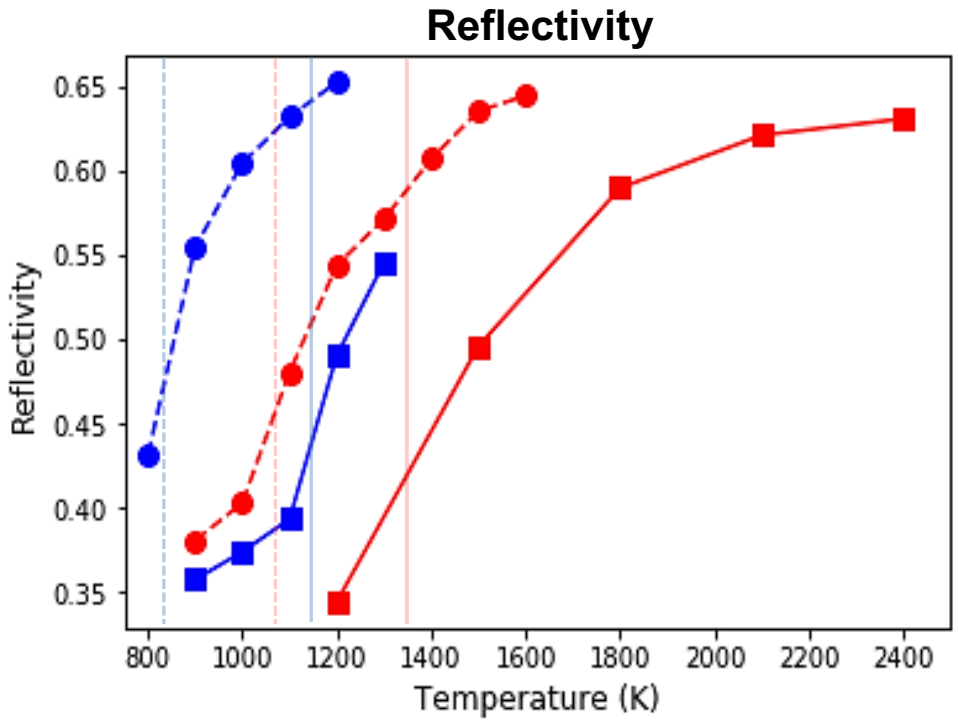
- Previous DFT studies have shown widely varying IMT's of hydrogen due to the choice of the XC functional.
- SCAN has the ability to accurately capture short and intermediate range van der Waals (vdW) interactions.
- SCAN-L, the deorbitalized version of SCAN, retains a similar level of accuracy at a fraction of the computational cost.
- The non-local correlation correction of rVV10 can further increase the accuracy of SCAN due to the inclusion of the long range vdW interactions.




J. Sun *et al*, Phys Rev Lett, 115, 036402 (2015).
R. Sabatini *et al*, Phys Rev B, 97, 041108 (2013).
D. Mejia-Rodriquez, S. Trickey, Phys Rev A. 96, 052512 (2017).

# A minimum dc conductivity of 2000 S/cm is used as the primary criterion to determine the temperature of the IMT for each isochore.

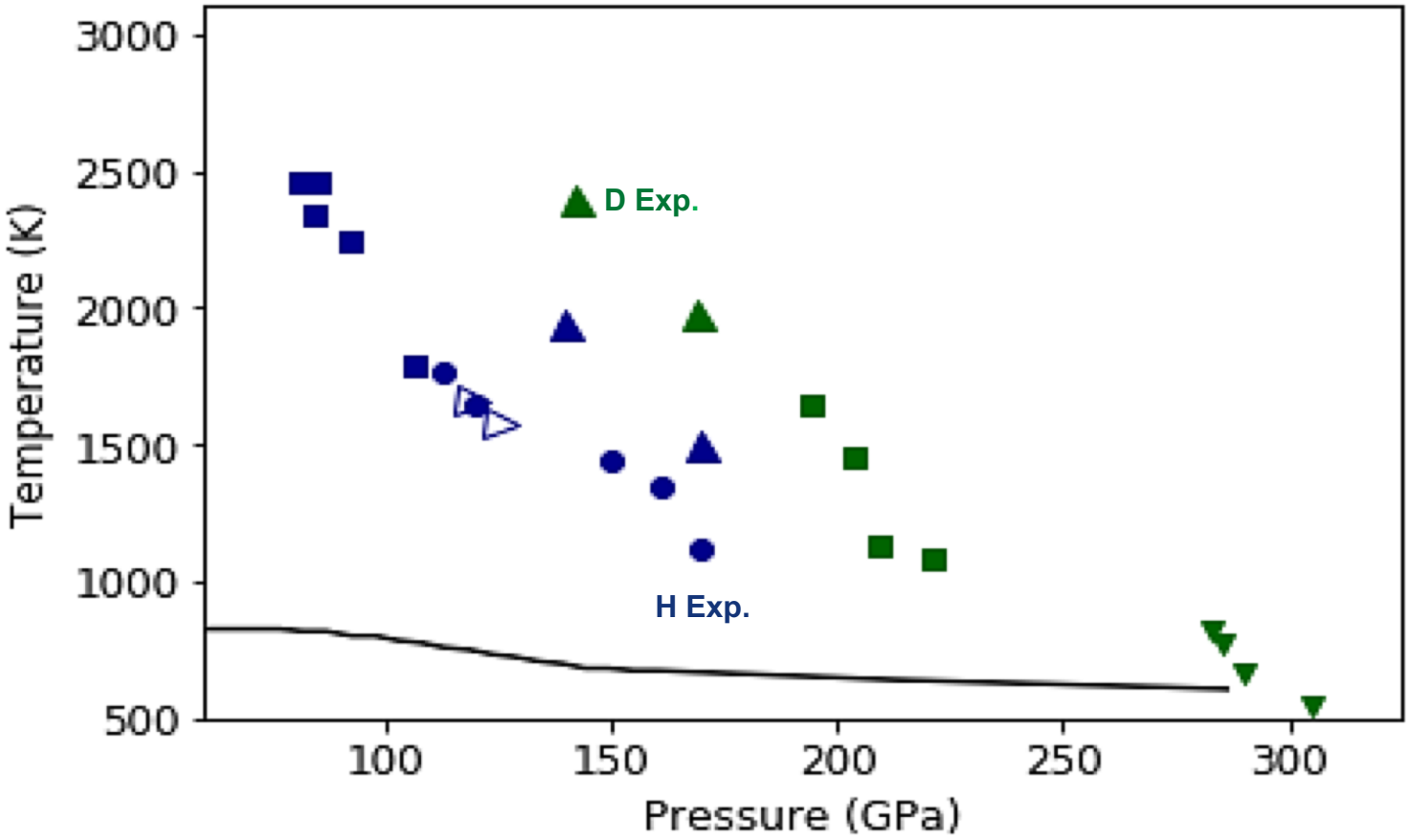



**The inclusion of NQE tends shift the IMT towards lower temperatures while producing a steeper slope in the dc conductivity and reflectivity at the onset of the transition**


R. Kubo, J Phys Soc Jpn, 12, 570 (1957).
D.A. Greenwood, Proc Phys Soc London, 71, 585 (1958).

# The resulting IMT boundary is in good agreement with previous experimental results for hydrogen across the PT space.





K. Ohta, *et al*, Sci Rep 5, 16560, 2015.
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V. Dzyabura, *et al*, Prac Natl Acad Sci USA, 110, 8040, 2013.

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M. Zaghoo, *et al*, Phys Rev B, 98, 104102, 2018.

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M.A. Morales, *et al*, Phys Rev Lett, 110, 065702, 2013.

P. C. Pierleoni, *et al*, Proc Natl Acad Sci USA, 113, 4953, 2016.
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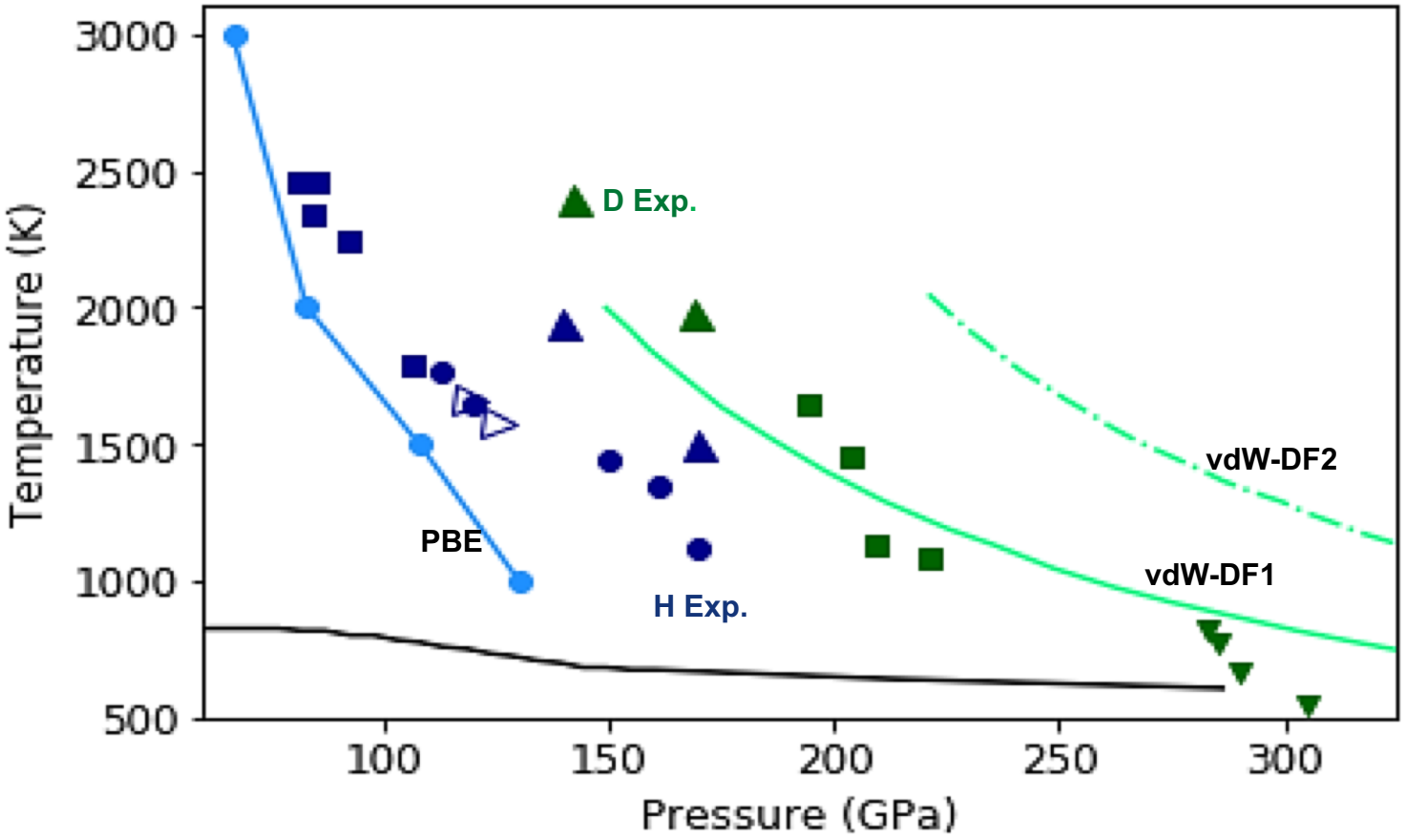



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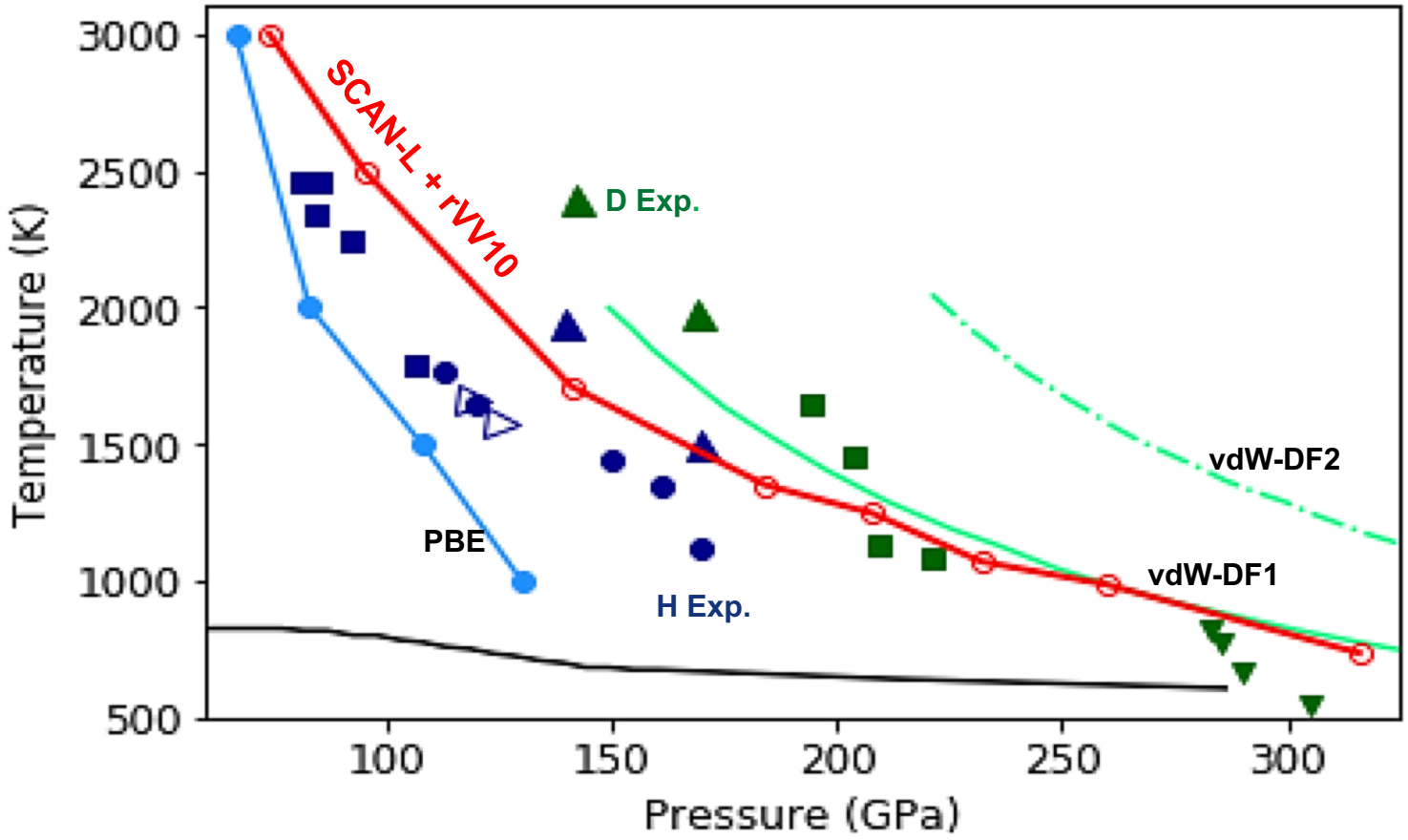



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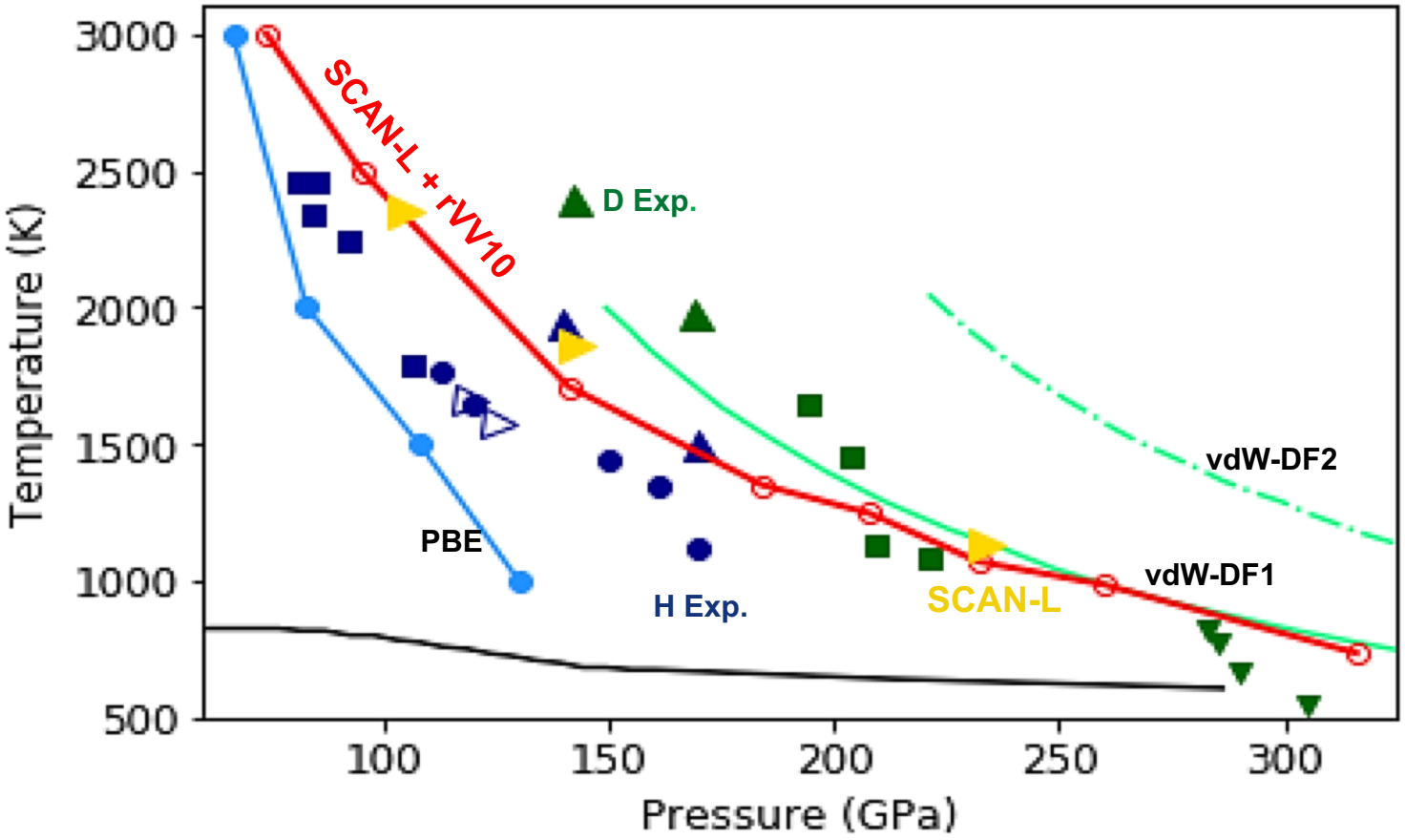



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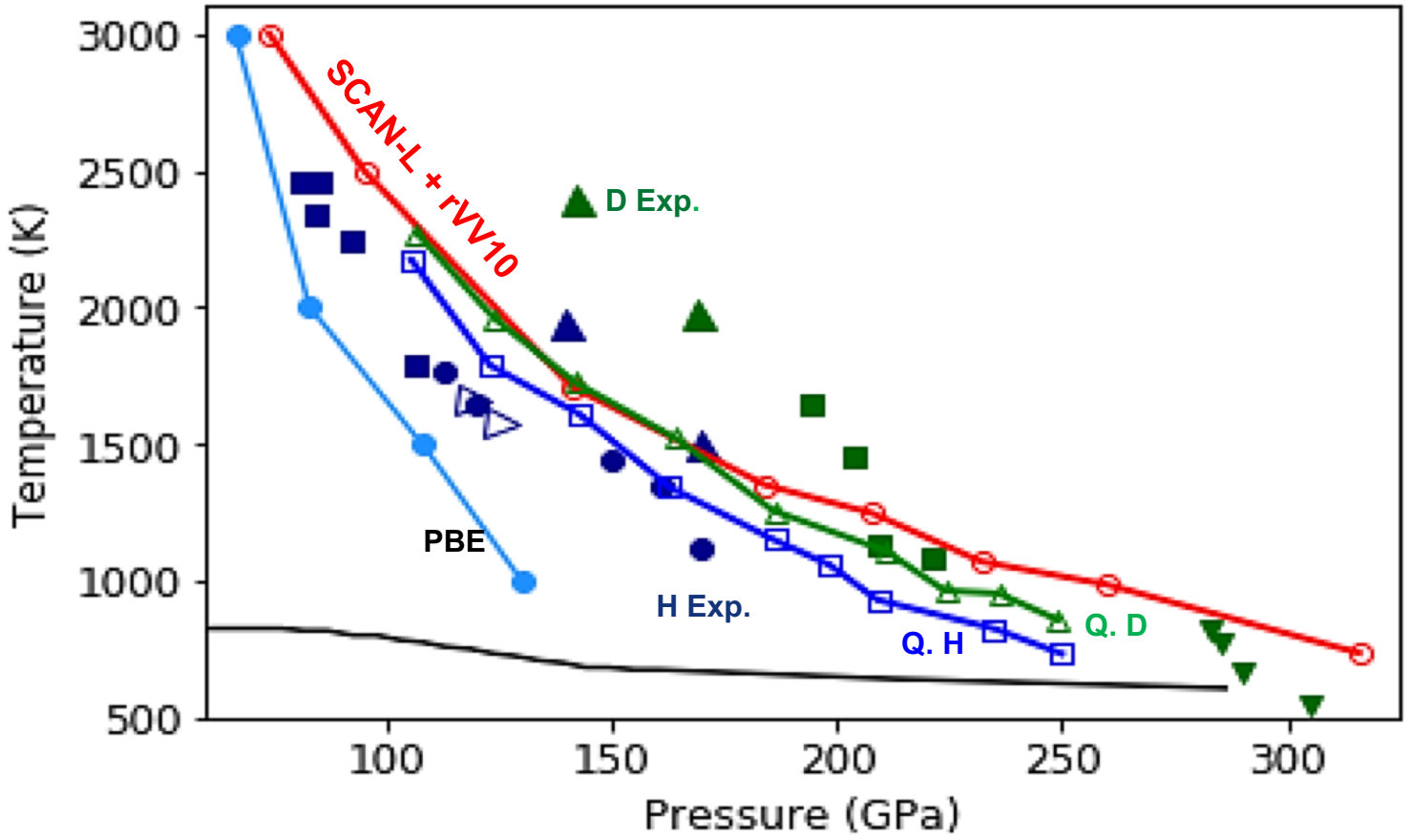



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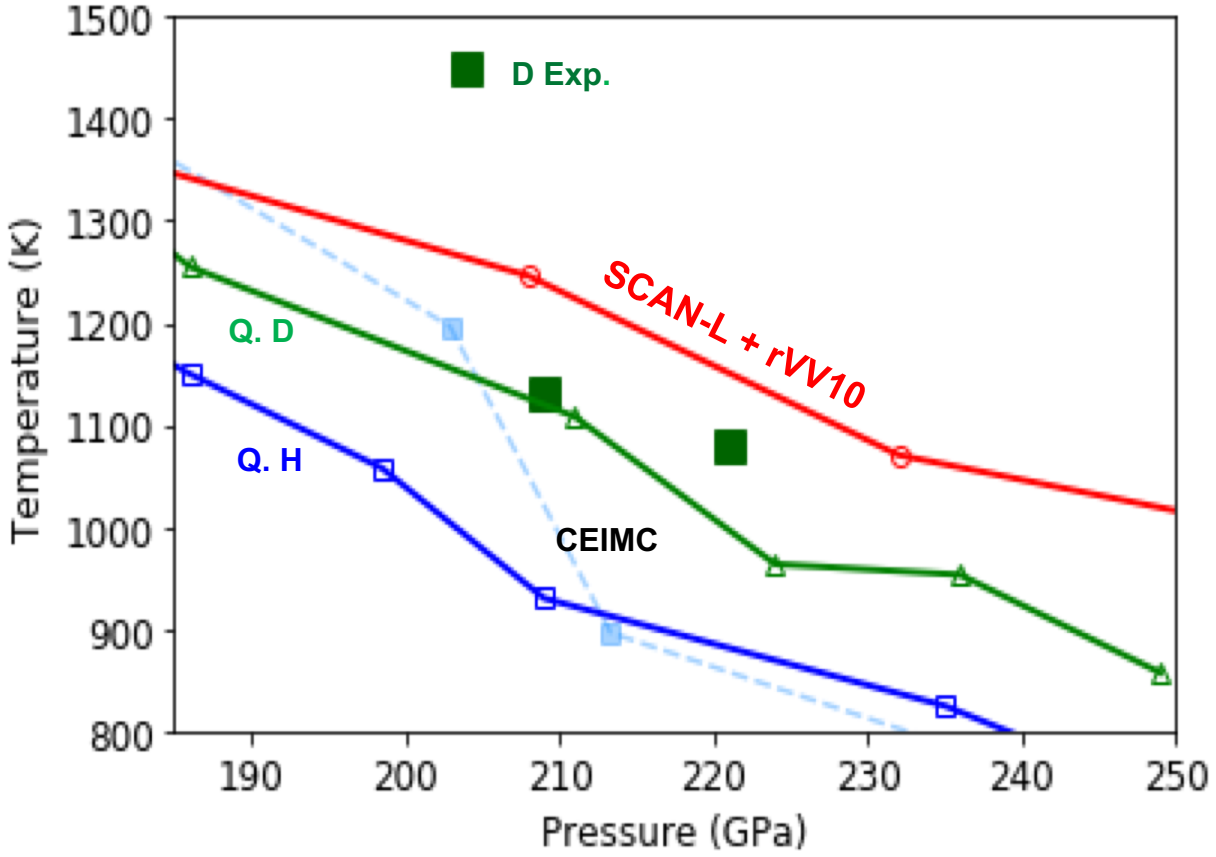
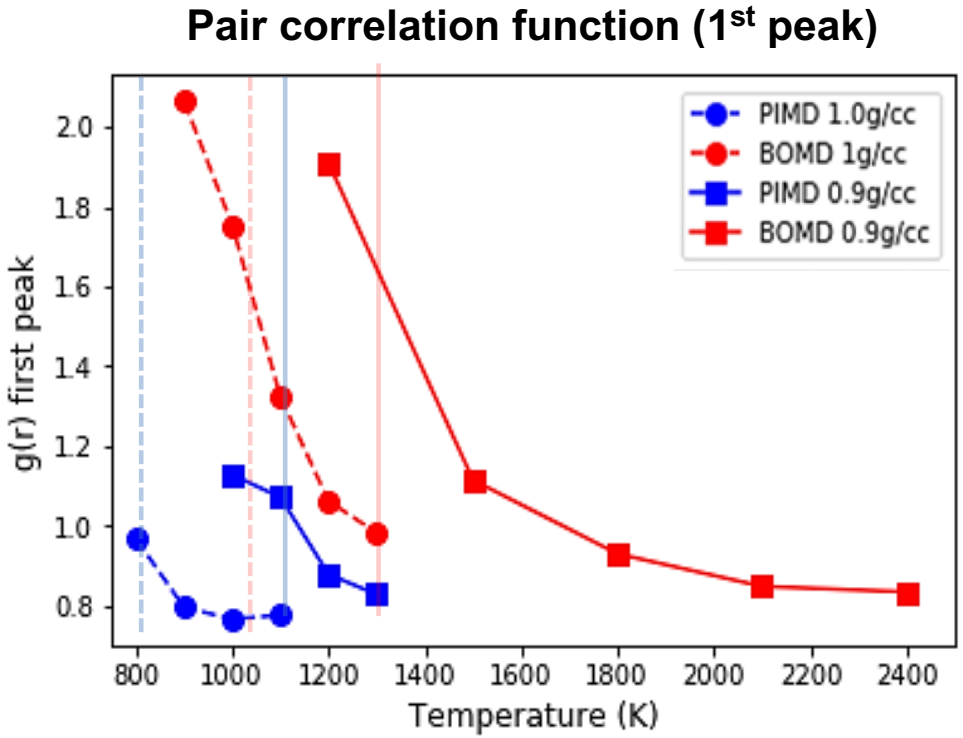
# With the inclusion of nuclear quantum effects an apparent step in the IMT boundary emerges.

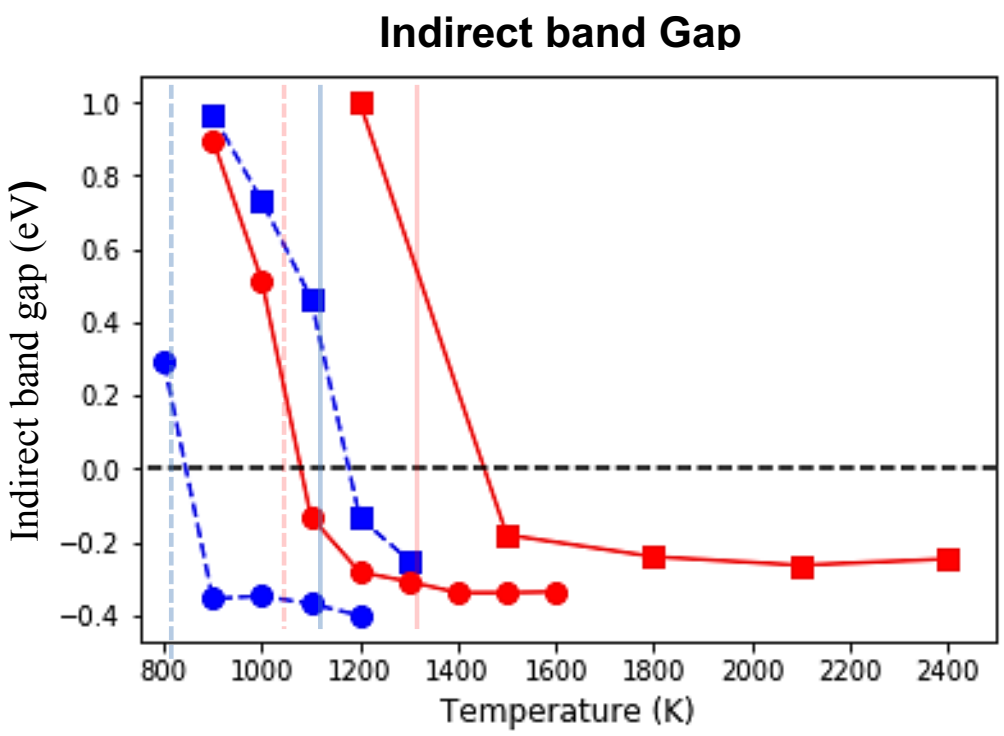



- The step like feature appears in CEIMC studies and potentially in experiment.
- This feature may be best explained by a change in the number of degrees of freedom for molecular hydrogen.

P. C. Pierleoni, *et al*, Proc Natl Acad Sci USA, 113, 4953, 2016.
P.M. Celliers, *et al*, Science, 361, 677, 2018.

# Analysis of the pair correlation function and the band gap provide further insights into the underlying mechanism of the metallic transition.




**These results support the notion that the IMT is driven by an abrupt closure of the band gap as a result of the dissociation of molecular hydrogen**

## Summary

# The insulator-metal transition (IMT) of fluid hydrogen has been determined through *ab initio* quantum molecular dynamic simulations with a metaGGA level exchange correlation (XC) functional.

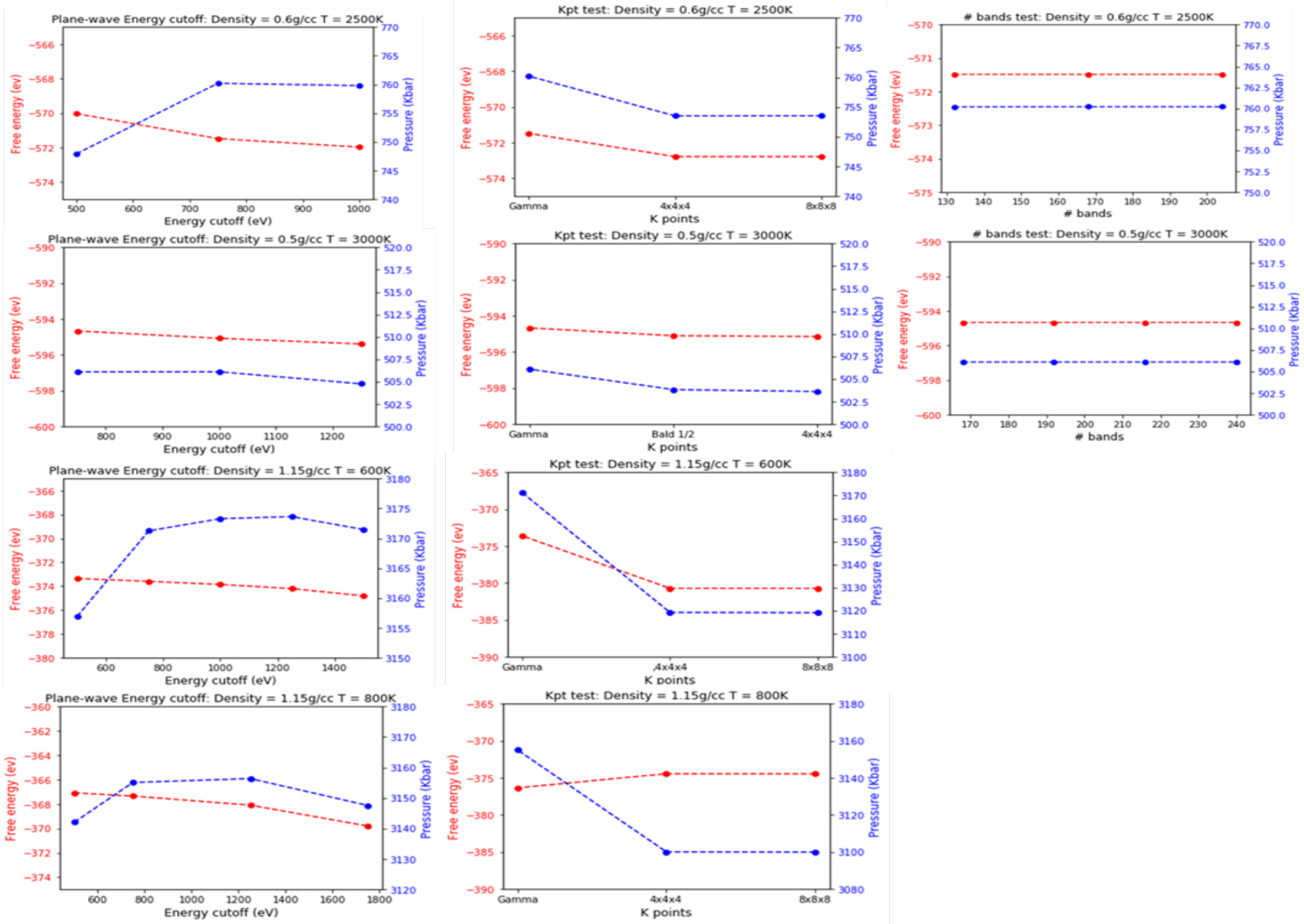
- **The resulting IMT is in better agreement with experimental measurements as compared to previous density functional theory studies.**
- **Analysis of the optical and structural properties of the system all show abrupt changes that coincide with the onset of a minimum metallic dc conductivity of 2000 S/cm.**
- **The inclusion of nuclear quantum effects significantly accelerates the dissociation of molecular hydrogen prior to the metallic transition resulting is a significant shift in the IMT boundary.**

**In total, these results support the idea of a metallic transition caused by an abrupt band gap closure directly associated with the dissociation of molecular insulating hydrogen into atomic metallic hydrogen.**

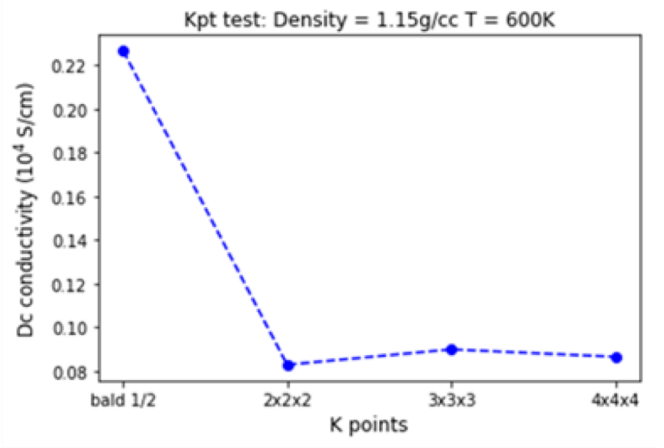
# Simulation Parameters

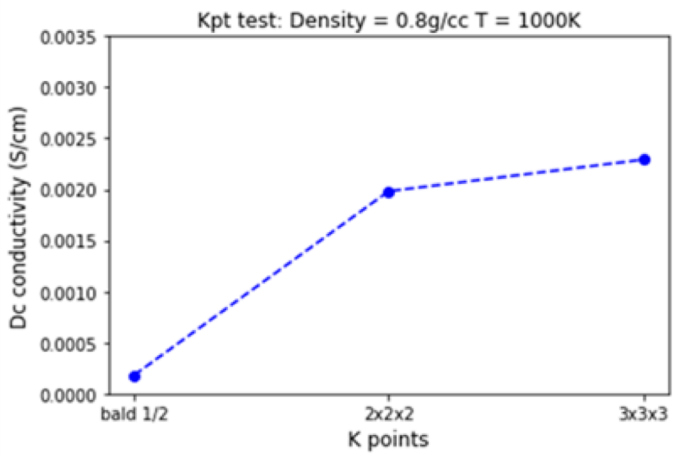
| Parameter | BOMD | PIMD |
|---|---|---|
| # atoms | 256 | 256 |
| Plane-Wave cutoff energy | 750 eV | 2700 eV |
| Electronic convergence criterion | 1E-5 eV | 2.7E-5 eV |
| # bands | 168 | 160 |
| K pt's | gamma | gamma |
| Time step | 0.1 fs | 0.2 to 0.5 (adjust for temperature and density) |
| # MD steps | 6000 | 6000 |
| Electron partial occupancies | Fermi smearing | Fermi Smearing |
| Bare protons | Projector Augmented Wavepotentials | Local |
| # beads | | 8 |

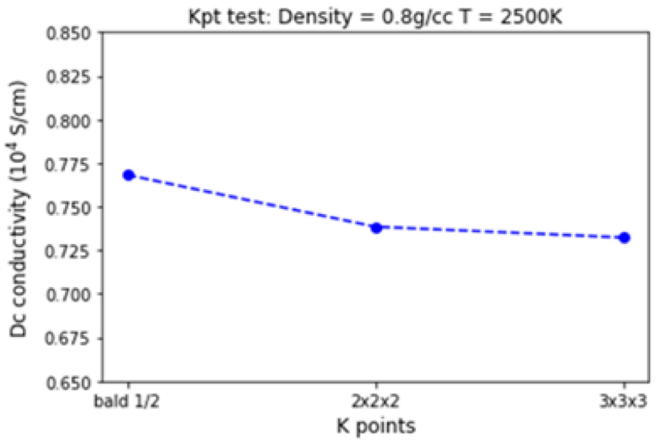
# MD convergence tests

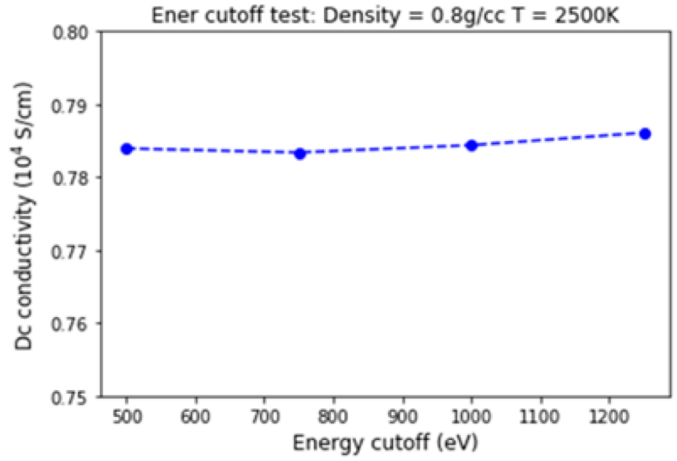


# Conductivity convergence tests

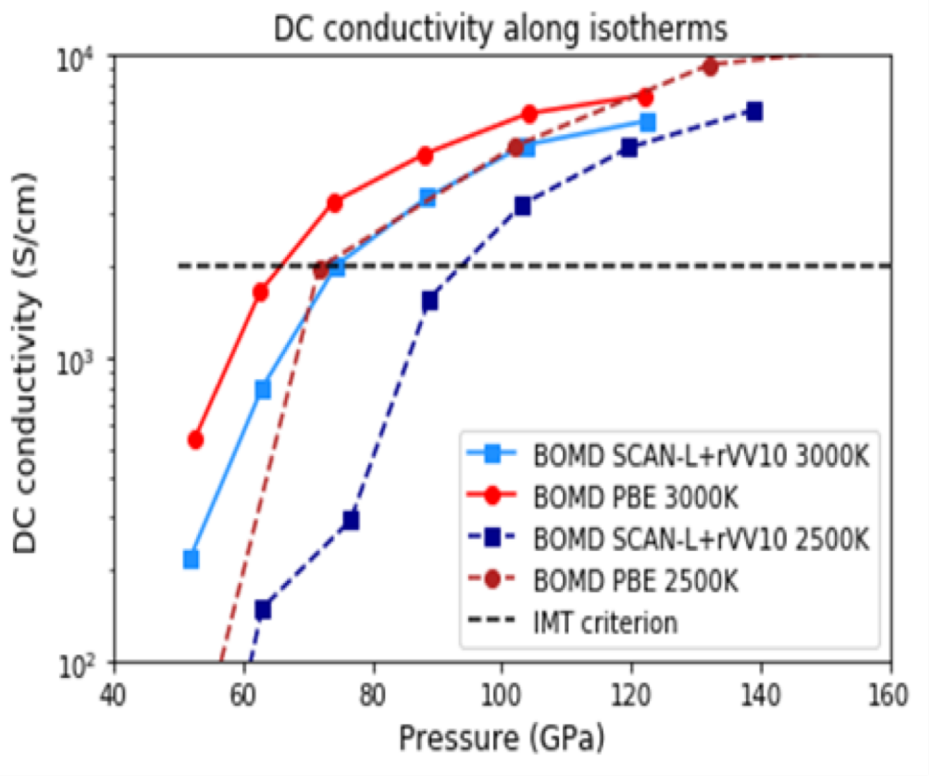


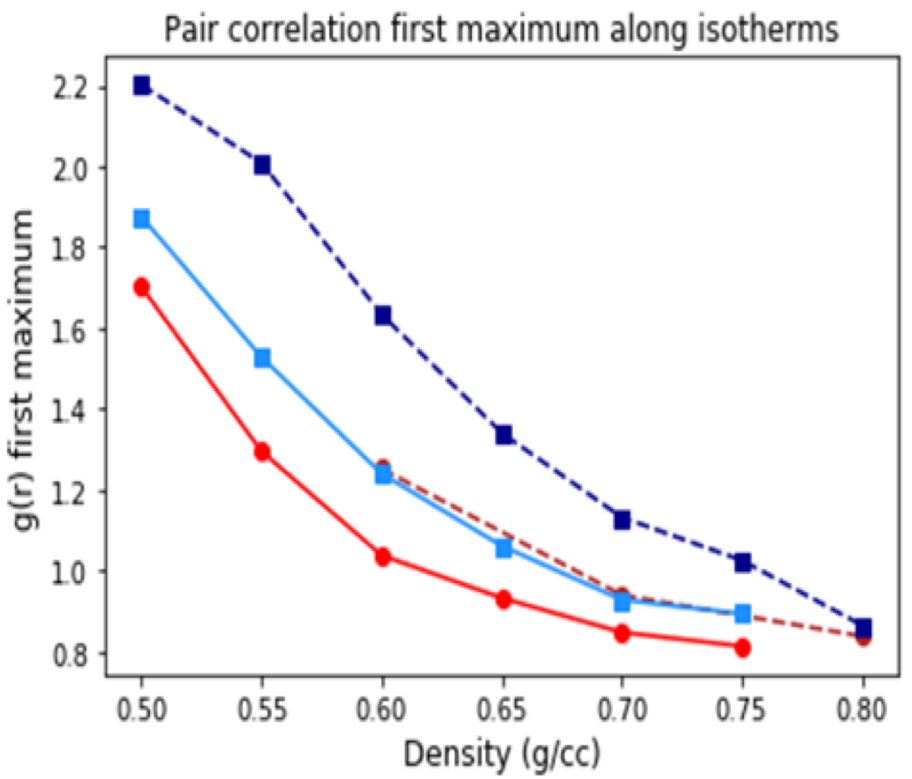



# PBE vs SCAN-L + rVV10 along the 2500 and 3000 K isotherms.



# SCAN + rVV10 vs SCAN-L + rVV10 ion configurations