

Limitations of Classical Molecular Dynamics with Quantum Pseudopotentials: The Role of the Pauli Exclusion Principle

Onegin A.S.^{1,2,@}, **Demyanov G.S.**^{1,2} and **Levashov P.R.**^{1,2}

¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow, 125412, Russia

² Moscow Institute of Physics and Technology, Institutskiy Pereulok 9, Dolgoprudny, 141701, Russia

@ onegin.as@phystech.edu

Classical molecular dynamics with quantum pseudopotentials—such as the Kelbg pseudopotential [1] and its improved version [2]—is widely used to simulate non-degenerate hydrogen plasma as a computationally efficient alternative to *ab initio* quantum methods. However, such approaches often fail to properly account for the Pauli exclusion principle, leading to unphysical results. In this work, we investigate the stability of hydrogen plasma across a coupling parameter range $\Gamma = 0.25$ – 2.5 using both standard and improved Kelbg pseudopotentials. We demonstrate that both approaches lead to system collapse at $\Gamma \geq 1.0$. The root cause is a violation of the Pauli principle: electrons with identical spin projections approach distances smaller than the thermal de Broglie wavelength, resulting in the formation of unphysical clusters. Analysis of radial distribution functions (RDFs) and energy evolution clearly reveals this artifact: an unphysical peak appears in the RDF for same-spin electrons at short distances when $\Gamma > 0.5$, while the potential energy exhibits a step-like decrease, indicating progressive collapse. Comparison with benchmark path integral Monte Carlo (PIMC) calculations [3] confirms the validity of both pseudopotentials only in the weakly coupled regime ($\Gamma < 0.5$). Our findings highlight the need for new models that explicitly incorporate quantum exchange effects and wavefunction antisymmetrization to accurately describe low-temperature plasmas.

We also discuss an empirical modification of the interaction forces [4], which stabilizes the system down to temperatures of ~ 1000 K, significantly extending the applicability range of classical molecular dynamics. Thermodynamic properties and plasma composition (H , H_2 , H_3^+ , H^-) are computed over a broad range of conditions. The behavior of the system at $T < 1000$ K is examined, where spatial homogeneity is lost: dense local aggregates form, confirmed by Voronoi diagram analysis. This indicates fundamental limitations of pairwise pseudopotentials even when explicit corrections for the Pauli principle are applied.

- [1] Kelbg G 1963 *Annalen der Physik* **467** 219–224
- [2] Filinov A V, Golubnychiy V O, Bonitz M, Ebeling W and Dufty J W 2004 *Phys. Rev. E* **70**(4) 046411 URL <https://link.aps.org/doi/10.1103/PhysRevE.70.046411>
- [3] Filinov A and Bonitz M 2023 *Physical Review E* **108** 055212
- [4] Demyanov G and Levashov P 2025 *arXiv preprint arXiv:2508.19820*