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Reliable PESs for Astrochemistry with autoPES: Methodology, Pitfalls, and Case Studies

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Reliable potential energy surfaces (PESs) are a prerequisite for astrochemical applications that rely on an accurate description of intermolecular interactions. In practice, the main bottlenecks are often not only computational cost, but also methodological and workflow issues: how to sample efficiently, choose a robust representation, and detect when an apparently smooth fit is physically wrong. In this lecture, I present a user's perspective on building reliable PESs with the autoPES[a] framework, focusing on common pitfalls, practical diagnostics, and lessons learned from case studies. Depending on the system size and the target accuracy, the reference electronic-structure data are generated using SAPT(DFT) and, when necessary, CCSD(T). Although autoPES provides powerful automation, it is not a black-box tool: reliable surfaces still require active user control. I therefore discuss practical safeguards: (i) consistent stitching between the long-range and intermediate-range regions, and (ii) protecting short-range behaviour through energy regularization and elimination of spurious holes (unphysical low-energy pockets) in the fitted PES.

To illustrate how these issues evolve with increasing complexity of the collision partner, I start from an atom collider (He), using CH_3CHO–He and benzonitrile–He as benchmarks that expose dispersion- and anisotropy-related fitting challenges.[b] I then move to a linear molecular collider (H_2), highlighting the methodological difficulties encountered for ion–molecule interactions on H_2Cl^+–H_2[c] and discussing ongoing PES development for benzonitrile–H_2. Finally, I consider a nonlinear polyatomic collider (H_2O), illustrated by CS–H_2O, HCN–H_2O, and CH_3OH–H_2O, with H_2O–HCN as a recent reference case.[d],[e]

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