Accelerating electronic resonance characterization through Gaussian Process Regression

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Electronic resonances are short-lived molecular species that decay by loss of an electron. They play an important role in processes such as DNA damage by low-energy electrons and astrochemistry. Their theoretical description requires the treatment of the electronic continuum in addition to the electron correlation. A common approach to account for the continuum in an electronic structure calculation, is to employ a Complex Absorbing Potential (CAP)[1,2], modifying the physical Hamiltonian H_0 into a CAP-augmented Hamiltonian:

$$H(\eta) = H_0 - i\eta W$$

where W is the CAP shape, usually chosen as a quadratic potential, and η its strength. An accurate determination of resonance energies and lifetimes depends on finding the optimal value of η, typically obtained through η-scans, by minimizing the log-velocity[3]:

$$\min_{\eta} \eta \left| \frac{dE(\eta)}{d\eta} \right|$$

where $E(\eta)$ represents the electronic energy of the system in the presence of the CAP.

This procedure typically requires more than 50 electronic structure calculations, depending on the range of η values scanned, which is one of the main limitations of the CAP method when studying large systems or using highly accurate electronic structure methods.

In this work, a novel approach using Gaussian Process Regression (GPR)[4] has been implemented in order to obtain the optimal value of η with fewer electronic structure calculations than with the conventional approach. Starting from two initial η values, a surrogate model is iteratively refined with new calculations, guiding the search toward the optimal value of η (Figure 1). Preliminary results with very well characterized electronic resonances like N_2^- and $C_2H_4^-$ show that the optimal η can be obtained in a fraction of the number of calculations needed in conventional scans, paving the way to efficient applications of the CAP method for resonances in larger systems.

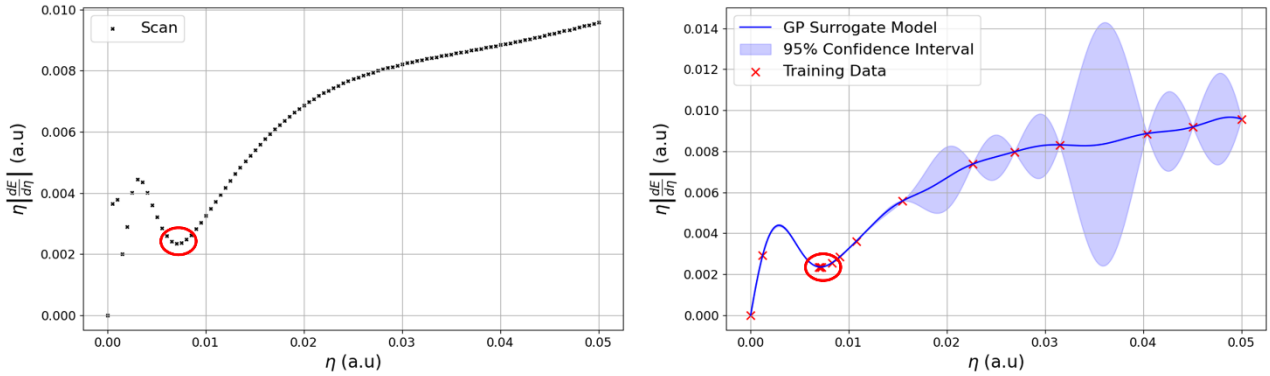

Figure 1.- Optimization of the η-value of N_2^- with the CAP-EOM-CCSD/aug-ccpvtz+3s3p3d method from $\eta = 0\ a.u$ to $\eta = 0.05\ a.u$ with a traditional scan (left, 50 points) and with the GPR algorithm (right, 14 points). The minimum is identified by the red circle.

References:

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