PÔSTER - RESUMO - DISPOSITIVOS ELETRÔNICOS, ELETROQUÍMICOS, SUPERCAPACITORES E BATERIAS

A GENERAL DFT FRAMEWORK FOR PREDICTING MOLECULAR REDOX PROPERTIES

Daniel Castilho De Oliveira Neto (dancastilhoneto@gmail.com)

Filipe Camargo Dalmatti Alves Lima (fdlima@ifsp.edu.br)

Reversible molecular redox systems play a central role in molecular electronics, electrochemical sensing, catalysis, and energy-conversion technologies.[1] In particular, organometallic compounds such as ferrocene are widely employed as internal standards in nonaqueous electrochemistry and as building blocks in electroactive materials. However, theoretical prediction of redox potentials in solution remains highly sensitive to methodological choices, solvation models, basis set selection, and thermodynamic corrections, often limiting reproducibility and quantitative comparison with experimental data.[2]

Here we present an ongoing density functional theory (DFT) study aimed at establishing a reproducible procedure for estimating redox potentials in solution, using ferrocene and substituted derivatives as model systems.[1] The protocol enforces strict methodological consistency across neutral and oxidized states by employing a thermodynamic cycle that combines adiabatic ionization energies, vibrational thermal corrections, entropic contributions, and solvation free energies to obtain solution-phase Gibbs free energies. The resulting free

energy differences are used to estimate relative redox potentials and to analyze substituent effects within a consistent theoretical framework.[3]

All molecular geometries are optimized and characterized through vibrational frequency analysis to ensure proper identification of stationary points. Solvation effects are included through implicit continuum models, enabling consistent treatment of different charge states in nonaqueous media. To reduce procedural variability and ensure traceability, an automated computational pipeline is being developed. The workflow standardizes input generation, geometry optimization, frequency calculations, extraction of thermochemical quantities, and conversion of free energies into redox descriptors, while recording all relevant numerical parameters to guarantee reproducibility. Calculations are performed using the ORCA quantum chemistry package.4

Preliminary results for ferrocene derivatives bearing electron-donating and electron-withdrawing substituents reproduce expected qualitative trends in ionization energies and relative redox shifts. Current efforts focus on systematic benchmarking against literature voltammetric data and on evaluating the impact of functional choice and solvation treatment on predictive accuracy.

This study seeks to establish a scalable and methodologically transparent computational framework for predicting molecular redox properties, with potential extension to other organometallic and organic electroactive systems relevant to advanced electrochemical and catalytic applications. Financial support provided by INEO, CNPq (408449/2024-1) and FAPESP (25/27044-5 and 23/17506-6).

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Palavras-chave: reversible molecular redox systems; redox potentials in solution; density functional theory; thermodynamic cycle; gibbs free energies; implicit solvation models; ferrocene and substituted derivatives; computational reproducibility; automated computational pipeline; molecular electrochemical properties.