Combining tuned range-separated hybrid functionals and Car-Parrinello Molecular Dynamics to obtain the solvated epinephrine UV-vis spectrum

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Abstract: Epinephrine is an amine belonging to the catecholamine group; it acts as a circulating hormone and neurotransmitter, and exists as an organic cation in the biological system. The interaction between drugs and water is fundamentally important to understand its absorption, transportation and biological action. There is a lack of theoretical studies that consider the aqueous solvation of neurotransmitter treating the solvent explicitly. After selecting 52 decorrelated frames of the ab initio dynamics made for the interaction between this catecholamine and water molecules studied through the Car-Parrinello Molecular Dynamics (CPMD), our goal was to study the UV-vis spectrum thereof. For this purpose, the LC-ωPBE tuned range-separated hybrid functional was used. In this calculation methodology, the electronic repulsion potential is separated into a long-range term (LR) and a short-range term (SR) and is given by:

\[
\frac{1}{r} = \text{erf}(\omega r) + \text{erfc}(\omega r),
\]

where \( \omega \) corresponds to the range-separation parameter. The adjusted \( \omega \) value found, enforcing Koopman's theorem, was \( \omega = 0.171 \text{ bohr}^{-1} \). Considering several frames of the dynamics the UV-vis bands near 227 and 280 nm was observed, approaching the experimental values more than theoretical results that consider the solvent implicitly, without the use of hybrid functionals and without parameter \( \omega \) adjustment. In a solvated medium, the epinephrine tends to protonation, which causes a \( n_O \rightarrow \pi_C^* \) charge displacement to the ring due to the polarization of the electronic density of the ring as a function of the dipole moment created by the protonation, leading to an inductive pulling effect in the direction of the protonated amine to stabilize the positive charge.

Key-words: epinephrine, UV-vis spectra, tuned range-separated hybrid functionals.

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References: