

## WHY ARE THE EXCITED STATES OF HETEROCYCLES STILL CHALLENGING FOR THEORY?

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Heterocyclic compounds are essential building blocks of biomolecules and systems that are highly relevant for optoelectronic applications. Surprisingly, even the lowest electronically excited states of heterocycles present a challenge for quantum chemical calculations.<sup>[1]</sup> This arises from the difficulty of providing a balanced description of excited states with very different characters, e.g., bright vs. dark, ionic vs. covalent, singly vs. doubly excited, etc. We analyse the origins of these excited state dichotomies from both molecular orbital and valence bond theory perspectives, using pseudosymmetry arguments that connect the two viewpoints.<sup>[2]</sup> We discuss the importance of electronic correlation for achieving a balanced description of excited states and explain why it is difficult, or even impossible, to reach high accuracy with conventional density-functional theory approximations. Finally, we delve into the origins of a less studied but recurring problem of valence-Rydberg mixing.

### REFERENCES

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