Isotopic computational device for probing molecular environments

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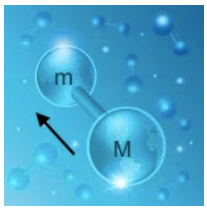
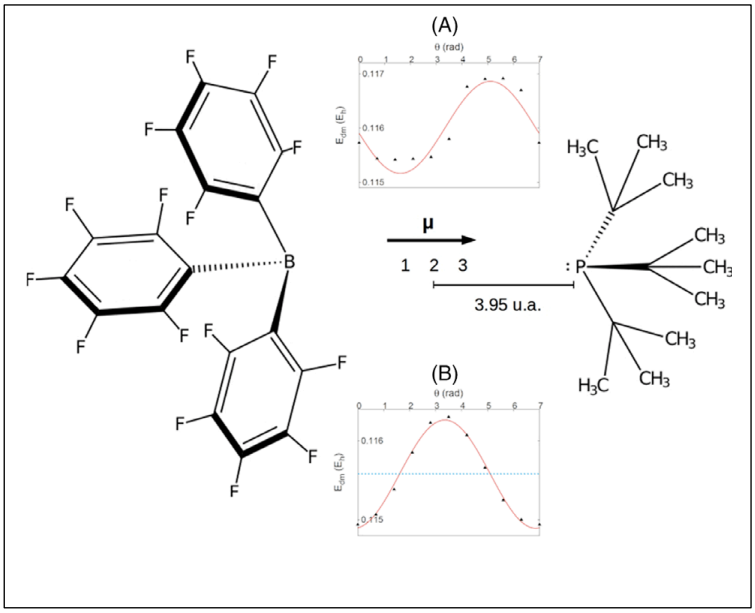
We propose the use of a fictitious isotopic probe, similar to the HD molecule, to investigate molecular environments, independently of an accurate representation of the electronic density and its gradient. HD has a small dipole moment, 0.0089 debye, due to its mass asymmetry. We explore the possibility of changing the nuclear masses in electronic calculations with our code ISOTOPE [1], to introduce the fictitious probe with a large and a small nuclear masses. We also freeze the internuclear distance so to create an appropriate dipole probe, with dipole moment of (typically) 0.086 debye.



Isotopic dipole moment μ

Once the probe "interacts" with a molecule, in an electronic quantum chemical calculation for the probe-molecule system, we subtract the Born-Oppenheimer energy from the total energy, so that the interaction energy is reduced to two classical terms: One from the interaction of the dipole moment with the molecular electric field and the other from the polarization of the molecule by the dipole, the second being usually much smaller than the first. These two energy terms can be identified and isolated either by rotating the dipole or by moving it away from the molecule and studying the consequent behavior of the interaction energy.

The probe can evaluate, for example, the vector electric field created by a molecule in chosen points. For this we just flip the dipole from its orientation of least energy (that gives the field direction), calculate the energy difference, and divide it by the dipole moment, obtaining the field strength. Applications are made for some molecules and to a frustrated Lewis pair (Fig. 1) [2], and to complexes showing π- and σ-hole bonds [3]. Presently, the probe is being used to investigate the cavities of fullerenes.



References

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2. Mohallem, J.R., Velloso, P.F.G., Arapiraca, A.F.C, International Journal of Quantum Chemistry e25917 (2019)
3. Velloso, P.F.G., Mohallem, J.R., International Journal of Quantum Chemistry e26116 (2020).

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