

# Dangers of the SCF-level DBOC: NO and NO<sub>2</sub> as examples

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The diagonal Born-Oppenheimer correction (DBOC) [1, 2], which accounts for the finite mass of the nucleus, plays a small but vital role in high-accuracy model chemistries such as HEAT [3–5], W4 [6], and others. The considerable complexity and expense of obtaining this correction with a correlated theory, such as coupled cluster [7], has encouraged most authors to evaluate the DBOC with Hartree-Fock, where it is comparatively easily obtained from the CPHF solutions [8] as per Handy *et al.* [9]. However, as has been previously demonstrated for force constants [10, 11], these solutions are a poor treatment of what may be considered the ‘SCF excited states’, and CPHF poles, where the CPHF solutions approach a singularity, are frequent troublemakers in quantum chemical calculations of radicals.

That the seemingly innocuous SCF-level DBOC, which depends on the CPHF solutions, is susceptible to the same problems as force constants is apparently not fully appreciated. Here, the NO and NO<sub>2</sub> radicals are used as case studies of such pathologies in the DBOC. The NO radical serves as an example of artificial fluctuations of the DBOC as a consequence of UHF instabilities, where better behavior is obtained at the CCSD and CCSDT levels of theory. The NO<sub>2</sub> radical demonstrates a true divergence of the DBOC at the crossing point of the <sup>2</sup>A<sub>1</sub> and <sup>2</sup>B<sub>2</sub> electronic configurations, where the adiabatic representation of molecules breaks down and model chemistries built within the Born-Oppenheimer framework should be treated with great care. Using these two examples, diagnostic tools for potential DBOC breakdowns will be presented.

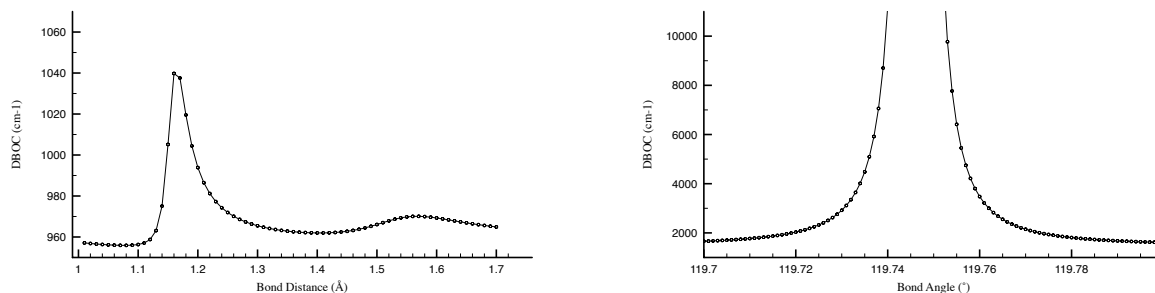


FIG. 1: Values of the DBOC (cm<sup>-1</sup>) as a function of bond length (Å) for NO (left) and bond angle (°) for NO<sub>2</sub> (right).

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