Development and Application of Dirac-Exact Relativistic Methods: Second Order Response Properties

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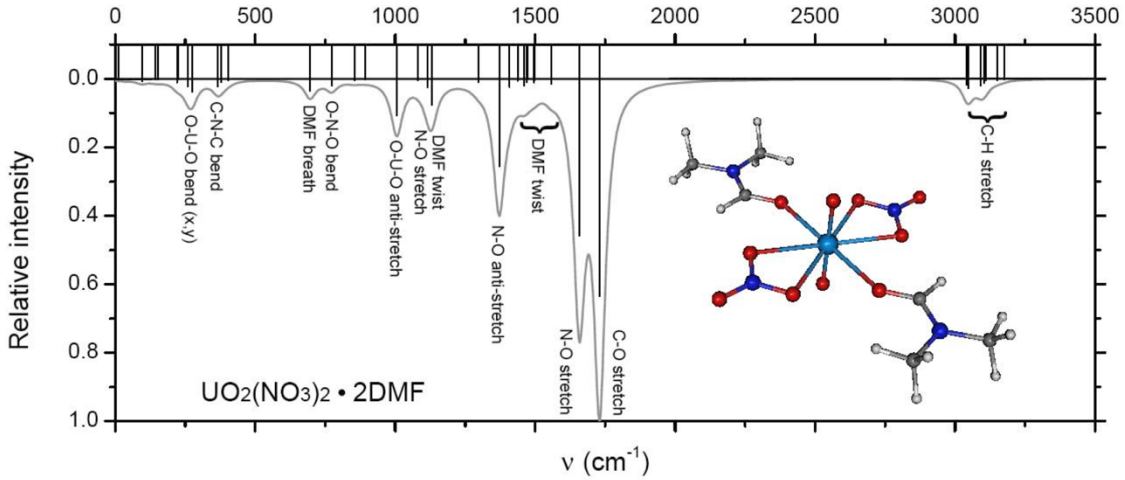
The Normalized Elimination of the Small Component (NESC) method, originally developed by Dyall and improved by Zou, Filatov and Cremer [1-6], is a first principles 2-component approach (positron components are eliminated) fully equivalent to the exact 4-component approach based on the Dirac equation. Since NESC provides the exact 2-component relativistic description of one-electron systems, it is an ideal starting point for developing a repertoire of methods by which first and second order response properties can be routinely calculated. In this work, we present algorithm and methods for the analytical calculation of second order response properties using both a spin-free and a two-component approach. In the figure, the calculated IR spectrum of $UO_2(NO_3)_2$•2DMF is shown as an example. We also discuss the impact of spin-orbit coupling on molecular properties. Applications are presented for mercury containing molecules and some other molecular systems containing transition metals, which require a relativistic treatment. Trends in calculated molecular properties are discussed in terms of spinor interactions involving the highest occupied and the lowest unoccupied spinors.



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