

Beyond the Born-Oppenheimer approximation by Coupled Cluster methods

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Enhancement of ab initio methods, in particular Coupled-Cluster (CC) methods allow the calculation of molecular properties with an accuracy which pushes the boundary of the Born-Oppenheimer approximation (BO). This is in particular true for binding energies, excitation energies, ionization potentials, structural parameters etc. On the other hand, we are now also able to treat processes associated with such electronic excitations which fall per se outside the boundary of BO approximation. After a short introduction into the joint treatment of electronic and nuclear coordinates, we will present two methods which enable us to perform calculations at the Coupled-Cluster level beyond the BO approximation.

The first one is the so called diagonal Born-Oppenheimer correction (DBOC) which considers the effect of the nuclear kinetic energy operator on the electronic wave function in an adiabatic fashion. Analytical formulae will be presented for use with general CC models. To reduce the computational resources required for the CC calculation of DBOC, a perturbational approach has also been developed. Calculations are reported to demonstrate the convergence of the DBOC with respect to electron correlation treatment and basis set as well as the accuracy of the perturbational approach.

The second method allows the calculation of the non-adiabatic coupling between electronic excited states at the Equation-of-Motion Coupled-Cluster Singles and Doubles (EOM-CCSD) level. Analytic formulae have been derived and implemented at the first time. Results are presented for the excitation spectrum of cytosine and pyrazine molecules showing that the coupling between the different states has an important effect on the spectrum.

Literature: [1] J. Gauss, A. Tajti, M. Kállay, J.F. Stanton and P.G. Szalay, *J. Chem. Phys.*, **125**, 144111 (2006). [2] A. Tajti and P.G. Szalay, *J. Chem. Phys.*, **131**, 124104 (2009).