Development potentials of the CASPT2 approach

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The CASPT2 and the MS-CASPT2 method, in it's all flavors, is today the standard method of choice for accurate molecular dynamics and spectroscopy simulations. However, already at the inception of the method in 1990, it was observed that the approach suffered from systematic errors – the approach underestimates the second-order energy correction of systems dominated by closed- shell configurations as compared to systems dominated by open-shell configurations. Furthermore, the standard CASPT2 zeroth order Hamiltonian invite possible difficulties and instabilities as expressed by intruder states. In this presentation we will review how this problem has been addressed, and to a large extent been resolved. These approaches, as shift techniques and modified zeroth order Hamiltonians, are standard in most applications today. One of the mostly used approaches is the so-called IPEA shift, an empirical corrections. Other corrects, as the G-family of corrections, are non-empirical. Recent benchmarking have strongly questioned the value of the IPEA shift, does it really make a significant difference? In this presentation we will offer an alternative to the IPEA shift, an approach void of any empirical parameters (for an example of the accuracy of the approach see Figure 1). This method, however, doesn't come without it's own problems. The presentation will conclude with suggestions on what problems further developments will will have to navigate around.

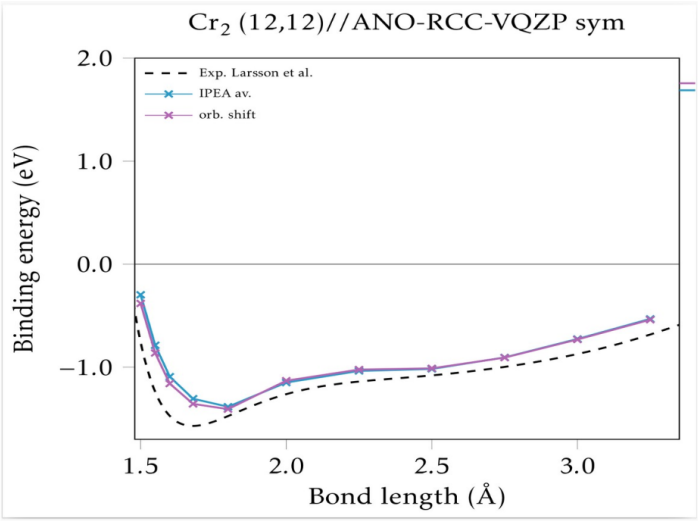

Figure 1: Non-empirical CASPT2 PES of Cr_2