Regularized CASPT2: an intruder-state-free approach

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Abstract

In this presentation we present a new approach to fix the intruder state problem (ISP) in CASPT2 based on σ^p regularization. The resulting σ^p-CASPT2 method is compared to previous techniques, namely the real and imaginary level shifts, on a theoretical basis and by performing a series of systematic calculations. The analysis is focused on two aspects, the effectiveness of σ^p-CASPT2 in removing the ISP and the sensitivity of the approach with respect to the input parameter. We found that σ^p-CASPT2 compares favorably with respect to previous approaches, and that different versions, σ^1-CASPT2 and σ^2-CASPT2, have different potential application domains. This analysis also reveals the unsuitability of the real level shift technique as a general way to avoid the intruder state problem.