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## Combined complete active space configuration interaction and perturbation theory applied to conformational energy prototypes: Rotation and inversion barriers

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A second-order multireference perturbation theory, termed as IVO-SSMRPT which allows the use of CASCI reference wave functions with improved virtual orbitals (IVO) for capturing static correlation and state-specific parameterization of the state-universal electronic wave function in an attempt to account for dynamic correlation has been utilized in an investigation of the torsional properties of ethylene, silaethylene, hydrogen peroxide, hydrazine, and oxalyl chloride. We also calculate the barrier to inversion of ammonia. IVO-SSMRPT is robust and useful to scan energy surfaces as it avoids the intruder-state problem, a troubling aspect of various established MRPT methods, without exploiting level-shifting or increasing the size of the active space. We find that IVO-SSMRPT with the use of a relatively small active space and basis set can be compared with recent reference estimates which are reproduced within the expected precision indicating the method is useful for the study of rotation and inversion barriers of challenging molecules.

PACS numbers:

**Keywords:** Multireference perturbation theory; Improved virtual orbitals; State-specific method; Torsional/Inversion surfaces; Barrier height.

### I. INTRODUCTION

Innumerable efforts have been made over the decades to account for the subtle and counter intuitive interplay of the static and dynamic components of correlation effects[1–4]. Computational methods in chemistry still struggle with the problem of yielding good accuracy in treating both correlations during the conformational changes in molecular systems. A balanced, and self-adaptive treatment of the weak (dynamical) and strong (static) correlations is absolutely essential to get a correct description. Molecular systems with stretched or twisted or partially broken bonds yield diradical character which are generally experienced as reaction intermediates. Due to orbital degeneracy, the wave functions of radicaloids contain various leading electronic configurations yielding multiconfigurational (MC) or multireference (MR) nature. To computationally describe reaction profiles and intermediates, we need to be able to describe MR situations. Though such a clear-cut distinction between correlations is questionable, both effects have rather unlike demands on the ansatz of the wave function. To account for nondynamical correlation effects, a wave function ansatz

is needed with high flexibility in configuration space in conjunction with low flexibility in one particle space. For describing dynamical correlation, a wave function ansatz capable of efficiently accounting for the changes in short-range interactions due to the presence of inter-electronic cusps in the true wave function is required. An efficient protocol for this is to tackle excitations out of a qualitatively correct, strongly correlated reference (MR) function. Several computationally cost effective schemes have been devised over the years based on a variety of ideas to handle dynamical correlation in MR problems [1–6].

The usual scheme to handle electron correlation effects in MR systems is to first execute a proper description of nondynamic correlation in a small subset of quasidegenerate orbitals, followed by a low-cost (naive) account of dynamical electron correlation in the remaining large set of core and external orbitals. Second-order MR perturbation theory (MRPT) is a particularly popular method of this class [see Refs. 5, 7 for details]. IVO-CASCI [improved virtual orbital (IVO) complete active space (CAS) configuration interaction (CI)] protocol[8, 9] is known to be one of the simplest variational approximations, which allows us to capture the main essence of static correlation in molecular systems in a robust and reliable fashion. IVO-CASCI is free of the convergence difficulties that often plague CASSCF [complete active space self-consistent field][10–12] computations. Unlike the CASSCF scheme, IVO-CASCI does not require iterations as it avoids the orbital optimization step altogether and is hence computationally cost effective. Note that the IVO-CASCI wave function retains all merits of the CASSCF one. In fact as that of CASSCF, the IVO-CASCI states

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