

Towards a Reduced-Scaling Method For Calculating Coupled Cluster Response Properties

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(GENERAL AUDIENCE ABSTRACT)

Since its inception, quantum mechanics has been widely used by theoretical chemists to study, model and predict a variety of molecular properties and reactions accurately and reliably. Central to the field of quantum mechanics is the Schrödinger equation, whose exact solution is only known for one electron systems. As such, numerous quantum mechanical models have been proposed over the years which attempt to solve the many body Schrödinger equation approximately. A very good example in this regard is the coupled cluster (CC) family of methods wherein the CCSD(T) model is considered as the “gold standard” of quantum chemistry due to its high accuracy. However, one major bottleneck which prevents the use of accurate CC models to study biological systems which routinely involve hundreds of atoms, is the issue of high computational expenses. For example, doubling the

system size in a CCSD(T) calculation can lead to a 64 times increase in the computational costs, which limits the application of this model to systems with 10 to 20 atoms. However, this unfavorable scaling with respect to system size is unphysical for large molecules as inter-electron interactions decay rapidly with distance, or are in other words, a local phenomenon. Reduced-scaling methods attempt to exploit this property of locality by finding a compact representation of the wavefunction. Various reduced-scaling approaches like projected natural orbitals (PNOs), projected atomic orbitals (PAOs) have been proposed and developed over the years which have extended the applicability of the CC methods to systems as large as proteins and DNA fragments. While these methods have been shown to be quite reliable for calculating properties like molecular energies, much more work needs to be done to guarantee similar levels of accuracy and computational cost for describing molecular response properties like polarizabilities and optical rotations. As the name suggests, response properties are related to the response or the change induced in the wavefunction in the presence of external electromagnetic fields like visible light. Accurate simulation of response properties like optical rotation is highly desirable as it can help the experimental chemists in understanding the structure-activity relationship of different drug candidates, an important part of the drug discovery process. However, limited applications of the reduced-scaling algorithms to these properties have been shown to yield large and often erratic errors.

In this work, we identify the reasons behind the unsatisfactory performance of the PNO based reduced-scaling approach for calculating response properties at the coupled cluster level of theory and propose novel modifications, which we refer to as PNO++, (A. Kumar

and T. D. Crawford. Perturbed Pair Natural Orbitals for Coupled-Cluster Linear-Response Theory. 2018, *manuscript in preparation*) which can provide the desired accuracy reliably at significantly lower computational costs than the regular PNO method. The motivation behind the PNO++ approach came from our works on the (frozen) virtual natural orbitals (FVNO), which can be seen as a precursor to the concept of PNOs (A. Kumar and T. D. Crawford. Frozen Virtual Natural Orbitals for Coupled-Cluster Linear-Response Theory. *J. Phys. Chem. A*, 2017, 121(3), pp 708-716) and the improved FVNO++ method (A. Kumar and T. D. Crawford. Perturbed Natural Orbitals for Coupled-Cluster Linear-Response Theory. 2018, *manuscript in preparation*). The essence of these modified schemes (FVNO++ and PNO++) lie in choosing a “field aware” representation of the wavefunction, which by construction, is much more compact than their conventional counterparts for calculating response properties. Thus, these schemes are ideal for applications to larger and chemically interesting systems like molecules in solutions, biomolecules, etc.