

Search for Accurate Non-perturbative Approximants to SS-MRCC

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In this talk, two useful nonperturbative approximants to the recently formulated state-specific multi-reference coupled cluster theory (SS-MRCC) will be developed and pilot numerical applications presented. The parent formalism is rigorously size-extensive and with the use of a complete active space leads to a size-consistent theory as well when localized orbitals are used. The method naturally obviates the notorious intruder problem when the target state energy is well-separated from the virtual functions. The wave operator in this formalism is of the Jeziorski-Monkhorst type, and, for a state-specific theory, this leads to redundancy of the cluster amplitudes. Imposing the twin requirements of size-extensivity of energy and the avoidance of intruders, the redundancy problem is resolved successfully. In the working equations, the cluster amplitudes for the operators acting on the different model functions are coupled. The two non-perturbative approximants suggested in this talk are designed to reduce the complexity of the working equations via well-defined nonperturbative approximations in two different ways. In the first variant, to be called the uncoupled state-specific MRCC (UC-SS-MRCC), we use an analogue of the anonymous parentage approximation in the coupling term, which leads to considerable simplification of the working equations, yet with very little deterioration of the quality of the computed energy. In the second variant, to be called internally contracted inactive excitations in SS-MRCC (ICI-SS-MRCC), the cluster amplitudes for all the inactive double excitations are regarded as independent of the model functions. Since the all-inactive double excitation amplitudes are the most numerous, this variant leads to a dramatic reduction in the total number of cluster amplitudes. Our pilot numerical applications on a host of molecules indicate that the ICI-SS-MRCC performs remarkably well, closely paralleling the performance of the rigorous SS-MRCC. While the UC-SS-MRCC uses equations closely resembling those in the parent theory, the variant ICI-SS-MRCC uses a manifestly contracted set of equations for the all-inactive double excitations.