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Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations

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(Received 23 October 2001; accepted 29 November 2001)

The convergence of the second-order Møller–Plesset perturbation theory (MP2) correlation energy with the cardinal number X is investigated for the correlation consistent basis-set series cc-pVXZ and cc-pV$(X+d)$Z. For the aug-cc-pVXZ and aug-cc-pV$(X+d)$Z series the convergence of the MP2 correlation contribution to the dipole moment is studied. It is found that, when d-shell electrons cannot be frozen, the cc-pVXZ and aug-cc-pVXZ basis sets converge much slower for third-row elements then they do for first- and second-row elements. Based on the results of these studies criteria are deduced for the accuracy of auxiliary basis sets used in the resolution of the identity (RI) approximation for electron repulsion integrals. Optimized auxiliary basis sets for RI-MP2 calculations fulfilling these criteria are reported for the sets cc-pVXZ, cc-pV$(X+d)$Z, aug-cc-pVXZ, and aug-cc-pV$(X+d)$Z with $X=$D, T, and Q. For all basis sets the RI error in the MP2 correlation energy is more than two orders of magnitude smaller than the usual basis-set error. For the auxiliary aug-cc-pVXZ and aug-cc-pV$(X+d)$Z sets the RI error in the MP2 correlation contribution to the dipole moment is one order of magnitude smaller than the usual basis set error. Therefore extrapolations towards the basis-set limit are possible within the RI approximation for both energies and properties. The reduction in CPU time obtained with the RI approximation increases rapidly with basis set size. For the cc-pVQZ basis an acceleration by a factor of up to 170 is observed. [DOI: 10.1063/1.1445115]