

CC2 excitation energy calculations on large molecules using the resolution of the identity approximation

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A new implementation of the approximate coupled cluster singles and doubles method CC2 is reported, which is suitable for large scale integral-direct calculations. It employs the resolution of the identity (RI) approximation for two-electron integrals to reduce the CPU time needed for calculation and I/O of these integrals. We use a partitioned form of the CC2 equations which eliminates the need to store double excitation cluster amplitudes. In combination with the RI approximation this formulation of the CC2 equations leads to a reduced scaling of memory and disk space requirements with the number of correlated electrons (n) and basis functions (N) to, respectively, $\mathcal{O}(N^2)$ and $\mathcal{O}(nN^2)$, compared to $\mathcal{O}(n^2N^2)$ in previous implementations. The reduced CPU, memory and disk space requirements make it possible to perform CC2 calculations with accurate basis sets on large molecules, which would not be accessible with conventional implementations of the CC2 method. We present an application to vertical excitation energies of alkenes $C_{2n}H_{2n+2}$, for $n=1-12$, and report results for the lowest lying dipole-allowed transitions for the TZVPP basis sets, which for $n=12$ contain 1108 basis functions. Comparison with conventional CC2 results for the smaller alkenes show that for CC2 ground state energies and for excitation energies of valence states, the error due to the RI approximation is negligible compared to the usual basis set error, if auxiliary basis sets are used, which have been optimized for MP2 energy calculations. © 2000 American Institute of Physics. [S0021-9606(00)31237-5]