The Divide-Expand-Consolidate Resolution of the Identity second-order Møller-Plesset perturbation theory method (DEC-RI-MP2)

Thomas Kjærgaard[a], **Patrick Ettenhuber**[a], **Kasper Kristensen**[a], **Simen Reine**[b], **and Poul Jørgensen**[a]

[a]*qLEAP - Center for Theoretical Chemistry, Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark;*[b]*Centre for Theoretical and Computational Chemistry, Department of Chemistry, Oslo University, Postbox 1033, Blindern, 0315 Oslo, Norway*

The Resolution of the Identity second-order Møller-Plesset perturbation theory (RI-MP2) method is implemented within the linear-scaling framework of the Divide-Expand-Consolidate (DEC) scheme.

In a DEC calculation, the full molecular calculation is replaced by a set of small independent fragment calculations. The number of independent fragment calculations scales linearly with the system size, rendering the method linearly scaling and embarrassingly parallel.

Like the DEC-MP2 method, the DEC-RI-MP2 method scales linearly with the system size, due to same number of fragment calculations. The individual fragment calculations scales with the fifth power of the number of basis functions for both methods. However, the DEC-RI-MP2 method has a reduced prefactor and is well-suited for implementation on massively parallel computeres.

The DEC-RI-MP2 method can be used with the occupied, virtual and Lagranian partitioning schemes within the DEC framework, which thereby provides three different ways of evaluating the correlation energy and an internal consistency check to validate the calculated correlation energy.

The DEC-RI-MP2 method may also be used to reduce the computational cost for the standard DEC-MP2 method, by preoptimizing the atomic fragments at the RI-MP2 level and provide accurate estimates of the pair fragment contributions.

The massively parallel implementation is described and applied to a set of medium sized molecules in order to perform a detailed error analysis, illustrating the error associated with the resolution of the identity. The DEC error control ensures that the standard RI-MP2 energy can be obtained to the desired precision.