Toward full-accuracy local correlation methods

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There are two basic ways of exploiting localization for electron correlation:
(1) Applying criteria that eliminate small but non-vanishing contributions from the outset, such as in the Saebo-Pulay and “triatomics in molecules” theories. These methods usually recover ~99 % of the correlation energy of full calculation. The truncation is (piecewise) differentiable, assuring smooth potential surfaces.
(2) Including all contributions above a small threshold. These methods rely on natural sparsity in an appropriate formulation, and are numerically equivalent to the full calculation. However, their cost is higher, and low thresholds are required to ensure smooth potential surfaces.

Most local correlation methods fall under category (1). However, methods of the second type have advantages: they avoid localization artifacts, don’t introduce a new model chemistry, and work, although with lower efficiency, for delocalized systems. Such methods are also required for testing methods of the first kind.

We will demonstrate that it is possible to take advantage of natural localization to yield a canonical MP2 method\(^1\) where the traditionally dominant computational cost, the first half transformation to MO basis, is low-scaling. This method has been effectively parallelized\(^2\) and analytical gradients have been implemented\(^3\). However, the second half transformation still has the O(N^5) scaling of the traditional canonical theory, although with a low prefactor. We have also developed a full-accuracy local correlation program\(^4\). It can be used for very large calculations (over 3000 basis functions on a single PC!) However, pair domains can be quite large (~300 projected atomic orbitals, PAOs). As stressed in Ref. 4, such large domains are wasteful for distant pair correlation. Based on a simple physical model, it can be shown that the virtual space for dispersion-type interaction can be described by a small molecular orbital basis for each localized occupied orbital\(^5\), in the limit, under certain simplifying assumptions, by three virtual orbitals for each localized occupied orbital. Using a molecular orbital basis ensures that the method is variational (in the Hylleraas sense), and avoids the difficulties with the multipole approximation of the integrals\(^6\). The new program, using a dispersion-adapted MO basis for distant correlation, will be described and first results presented\(^7\).

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5. W. Meyer, private communication.