

Local Correlation Models

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Abstract. Local correlation models that meet the requirements of a theoretical model chemistry are discussed. Two types of models are considered. The first class uses a valence active space that associates one correlating orbital for each occupied valence orbital. In these models the fundamental quantity is the electron pair; even the simplest local approximation (perfect pairing) exactly treats an isolated electron pair in this active space. The second class of models uses no active space. In this case we argue that the most appropriate fundamental quantity is the atom; even the simplest local approximation (atoms-in-molecules) exactly treats an isolated atom.

1 Introduction

Theoretical chemical models are systematic approximations to exact quantum mechanics that traditionally involve two approximations. The first one is a limited treatment of electron correlation. Within wavefunction-based theory this has evolved into a hierarchy that goes from Hartree-Fock (HF) theory (no correlation) to MP2 theory (perturbative 2-electron substitutions), to singles and doubles coupled cluster theory (CCSD; self-consistent 2-electron substitutions), and finally to perturbative inclusion of 3-electron correlations via CCSD(T). The second approximation, of course, is the selection of a limited atomic orbital expansion space.

While the correlation treatments mentioned above are convergent in accuracy (at least in most usual applications), they increase in cost as M^5 (MP2), M^6 (CCSD), and M^7 (CCSD(T)), as a function of molecule size M . It is clearly highly desirable to reduce these high computational cost scalings. As electron correlation is primarily a short-range phenomenon, arising from the electron-electron cusp, this is possible by imposing spatial truncations, forming the basis of low-scaling local correlation methods. The modern era of local correlation research was initiated with the work of Pulay, and Pulay and Sæbø [1], with subsequent important extensions by many others.

In principle, local correlation approximations can be made at a sufficiently conservative level that numerical results (and thus the theoretical chemical model) are unaffected. In practice, however, this approach is probably too conservative, and thus, led by the ideas of Pulay and Sæbø, much work has been performed on local correlation

approaches that recover a large percentage, though not all, of the correlation energy of a given approximated theory. Great numerical success has been achieved, including linear scaling of computation with molecule size [2]. However, the Pulay-Sæbø approach fails to be a well-defined theoretical chemical model, because it depends on one or more numerical parameters to define which occupied orbitals are correlated by which unoccupied orbitals. Connected with this issue, it fails to yield properly continuous potential energy surfaces, and therefore has not found major application in geometry optimizations.

In this article we discuss alternative local correlation models that do satisfy the requirements of a well-defined theoretical model chemistry. In our opinion, these are:

i) The theory should be uniquely defined for any nuclear configuration without any adjustable parameters, such as thresholds, cutoff lengths, or selection criteria, that affect the result.

ii) The theory should yield potential energy surfaces that are strictly continuous so that chemical reactions can be studied.

iii) The theory should yield additive energies when applied to non-interacting systems (size consistency property).

iv) The theory should possess a reasonable degree of accuracy and feasibility. Clearly more accurate models tend to be less feasible for application to large molecules.

2 Valence Active Space Models

We choose to begin our discussion of local correlation models by assuming that electron correlation is treated not in the full correlating space of all empty (virtual) orbitals, but rather in a limited space of valence orbitals that are divided into a nominally occupied set and a matching set of nominally empty orbitals [3]. The occupied and empty orbitals are paired such that there is a 1:1 association between each occupied orbital j and each corresponding empty (correlating) orbital j^* . As a result an isolated electron pair can be exactly described by a 2-configuration wavefunction, where the two orbitals, and the excitation amplitude, are to be optimized.

The important thing is that a valence active space of this type (or simple generalizations that associate 2 or 3 or n correlating orbitals with each occupied orbital) partitions the orbital set into spatially localized functions that describe individual electron pairs separately without repetition or duplication. This contrasts with the situation when no active space is introduced: then the same virtual functions are usually called on to describe intrapair correlations in a number of nearby pairs.

The simplest valence active space local correlation model is the one that treats intra-pair correlations exactly, and at the same time completely neglects all interpair excitations. This is the perfect pairing (PP) model; where the number of 2-electron substitutions is just linear in the size of the system:

$$\hat{T}_{PP} = \sum_i^{\text{valence pairs}} t_i a_{i^*}^\dagger a_{i^*}^\dagger a_i a_i \quad (1)$$

In the context of coupled cluster theory, it was first explored by Cullen in the chemical literature [4]. PP can also be generalized to permit nonorthogonal orbitals [5], which can overcome some symmetry-breaking artifacts for molecules with multiple resonance structures. Note that the PP model is defined completely without parameters. Furthermore all orbitals are optimized to minimize the energy. Physically the merit of the PP model is that it exactly describes the making and breaking of any (or each) individual electron-pair bond within the valence active space. As molecules are collections of interacting electron pairs, this is clearly a logical starting point for local correlation modeling.

The next logical level of local correlation must include 2-electron excitations that also couple together different electrons pairs. 2-electron excitations that couple together two electron pairs without net transfer of electrons are the leading contributions of this type. Such excitations are responsible for the long-range van der Waals interactions between separated electron pairs. It is likely also to be the dominant part of short-range pair-pair correlations also. The model which adds these correlations has been somewhat whimsically defined as “imperfect pairing” (IP) [6]. It increases the number of 2-electron correlations from linear in the PP model (intra-pair only) to quadratic, and thus also necessarily increases the computational complexity. At the present stage [7], its computational cost scales approximately with M^3 , which is roughly the square root of growth of the full theory including all 2-electron correlations in the valence active space.

It remains somewhat less certain as to how best to define a third level of local correlation modeling in the valence space. At present we are exploring the inclusion of inter-pair correlations that account for the two possible types of single electron transfers between pairs, as a result of correlated fluctuations. The first type, which might be called “charge coalescence”, begins with separate electrons in occupied levels of two different pairs, and excites them into the correlating orbital of just one pair. The second type, “charge splitting”, begins with both electrons in the occupied level of a single pair and promotes them into two correlating levels one of which is on the same pair, and the other on a different pair. This level of theory could be defined as “singly ionic pairing” (SIP).

$$\hat{T}_{SIP} = \hat{T}_{IP} + \sum_{ij}^{pairs} \left\{ t_{ij}^{i^* \bar{j}^*} a_{i^*}^\dagger a_{\bar{j}^*}^\dagger a_{\bar{j}} a_i + t_{\bar{i}\bar{j}}^{i^* \bar{j}^*} a_{i^*}^\dagger a_{\bar{j}^*}^\dagger a_{\bar{i}} a_j \right\} \quad (2)$$

An alternative is to additionally include 2-electron transfers between electron pairs or doubly ionic pairing (DIP).

2-electron excitations also exist that couple together more than two electron pairs. In particular the most general excitations couple together 4 pairs. We shall not concern ourselves with 3-pair couplings in this work. We shall use results based on the full 2-electron substitution operator as a benchmark against which to test the simpler approximations later. This full theory is then valence optimized doubles (VOD) [8].

3 Full Space Models

We turn next to the formulation of local correlation models for the electron correlation operator when no active space is in use. The localized orbitals spanning the full virtual space are very effectively defined (that is with very small fractional redundancy) by projecting the atomic orbitals (AO's) into the virtual space with $\mathbf{1-P}$, where \mathbf{P} is the 1-particle density matrix. This, for a large molecule, automatically gives atom-centered functions spanning the virtual space, with the same locality properties as \mathbf{P} (which of course is exponentially localized for insulators). Furthermore, these functions are also atom-labeled as they derive from the atom-labeled AO's via a direct mapping. So, while the virtual functions in the case of the valence active space partitioned naturally amongst the electron pairs (one per pair), here they partition naturally by atoms.

This suggests that we should build up a set of local correlation methods starting with an atomic partitioning of the orbitals and thus the correlation contributions. To make such a partitioning possible, we also need to partition the occupied orbitals amongst the atoms. Except for such uninteresting special cases as noble gas clusters, an atomic partitioning is not possible with orthogonal orbitals because bonding occupied orbitals are intrinsically shared between atoms. Therefore an over-complete (and thus non-orthogonal) set must be used to describe the occupied space. The least over-complete set that we could use is a minimal atomic orbital basis, which gives each atom a number of functions equal to the sum of its core and valence atomic orbitals. While these orbitals could be defined using some independent definition (such as "extracted polarized atomic orbitals") it is clearly best if they are defined to minimize the local correlation energy, just as the occupied and virtual functions defining the valence active space were optimized in the previous section.

The simplest full space local correlation model can now be defined as "atoms-in-molecules" (AIM). First, we express the correlation operator (for whatever method we are developing the local correlation model) in the combined minimal occupied and full virtual atomic representation discussed above. Then all correlation amplitudes that are localized entirely on a single atom are retained, while all correlation amplitudes coupling together two or more atoms are discarded. This model is manifestly exact for an isolated atom (or an ensemble of isolated atoms), and is the most drastic local correlation that is sensible.

Note that no parameters enter, and the AIM model meets all the criteria of a well-defined theoretical model chemistry. No results have been reported with the AIM model hitherto, and so, in the following section, one of our main objectives is to assess its performance on a judiciously chosen model problem. There are only a linear number of degrees of freedom in the AIM model, and so high-performance low-scaling implementations should be possible. This work is in progress for MP2 and orbital-optimized CCD (OD), for which the correlation operator then takes the form:

$$\hat{T}_{AIM} = \sum_A^{atoms} \left\{ \sum_{i \in A}^{occ} \sum_{j \in A}^{occ} \sum_{a \in A}^{virt} \sum_{b \in A}^{virt} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \right\} \quad (3)$$

We view AIM as the most reasonable analog of PP for the case when correlation is allowed in the full space.

The next logical level of local correlation modeling is to include those correlation amplitudes that couple together pairs of atoms, but without permitting net electron transfer between them. At the level of 2-electron excitations (correlations), this model, “diatomics-in-molecules” (DIM) fully recovers long-range correlation. It has already been explored [9] and quite efficiently implemented (M^3 scaling) for large-scale MP2 calculations. However the minimal atomic orbitals were not fully optimized, which is desirable in future work.

More complete 2-center local correlation models can also be defined, but has not been explored hitherto, primarily because of implementation challenges that have not yet been fully overcome. Disregarding practical challenges for the present, it is logical to next include the two classes of two-center terms responsible for single electron transfers between atoms. There were previously referred to as “charge coalescence and charge splitting in the previous section. This model will also be assessed in the following section via calculations on a toy system. Applied to double (2-electron) excitations, it includes all 2-center amplitudes apart from those that excite 2 electrons from one atom to another. They are omitted because they are clearly associated with basis set superposition effects: two electrons from one atom are correlating their motion by “borrowing” virtual functions from another atom.

Three-center models are also possible, and we have explored them with some success in other work [9]. However we shall not consider them further here.

4 Calculations on a Toy Model

To provide some assessment of how the different local correlation methods discussed in the previous sections perform, we shall consider some pilot calculations on a simple toy model system. It consists of 8 H_2 molecules, each arranged at the center of the sides of an octagon. Each intra-molecular H-H distance has its standard value of 0.74 Å, while the intermolecular spacing is variable. The 6-31G basis was used for the calculations, and the calculations were performed with test codes that were attached to the Q-Chem program package [10].

The results of local MP2 calculations using various local models discussed above are presented in Table 1, as a function of intermolecular spacing. The quantity reported is the percentage of the full MP2 correlation energy recovered by each local correlation method. We note that all local models are exact for isolated H_2 molecules, and thus the interesting regime is the transition from highly localized electronic structure (nearly non-interacting H_2 molecules) towards more and more de-localized electronic structure. At the same time, in terms of electron correlation we are changing from well-separated electron pairs completely dominated by intra-pair correlation towards less and less distinct sets of pairs, where inter-pair correlations are becoming stronger in both absolute and relative senses. So, while these are toy calculations, they can still pose a challenging test for local correlation methods.

Table 1. Local MP2 calculations using the AIM, DIM, and DIM+SI models. The results are expressed as percentage recovery of the full MP2/6-31G correlation energy for this system, which is a ring of hydrogen molecules, with various intermolecular spacings. To roughly characterize the electronic structure of the system at each separation, the bandwidth and bandgaps obtained with canonical Hartree-Fock orbitals are also reported. All calculations used a minimal basis of modified atomic orbitals to span the occupied space

R / \AA	1.9	1.5	1.2	1.0	0.8
$E_{\text{HOMO}}-E_1$ /eV	2.72	5.58	9.63	13.88	20.11
$E_{\text{LUMO}}-E_{\text{HOMO}}$ /eV	19.27	17.74	15.37	12.73	8.76
AIM /%	95.87	91.23	83.22	74.94	65.28
DIM /%	99.36	98.73	97.82	96.82	95.12
+ singly ionic /%	99.84	99.49	98.85	98.21	97.31

A quite rapid convergence of the results towards 100% is seen for this hierarchy of 3 models. The very strongly truncated AIM model still recovers clearly the leading contribution of electron correlation. It is quite possible that this will be a useful starting point for the development of local coupled cluster methods. The DIM model then recovers a substantial majority of the correlation neglected by the AIM model, substantiating its value as the next level of model. Singly ionic pair terms in turn cover a majority of the remaining discrepancy in this model system. Roughly we estimate that stable molecules might correspond to roughly between 1.2 and 1.5 in this toy system.

Table 2. Local valence coupled cluster doubles calculations using the PP, IP, SIP and DIP models. The results are expressed as percentage recovery of the full VOD/6-31G correlation energy for this system, which is the same as used for Table 1. All calculations used the PP orbitals

R / \AA	1.9	1.5	1.2	1.0	0.8
PP /%	97.9	93.9	85.9	75.6	60.0
IP /%	99.1	96.4	90.6	82.4	75.4
SIP /%	99.9	99.3	97.1	92.6	82.8
DIP /%	100.0	99.5	98.0	94.8	87.4

In Table 2, we summarize a similar series of calculations on exactly the same systems, but this time using valence coupled cluster methods truncated with the local correlation models discussed in Sec. 2. These results are generally similar to those reported in Table 1. PP, containing just a linear number of degrees of freedom, nevertheless recovers the leading correlation contributions. IP is perhaps slightly less successful than DIM at correcting for the missing correlations, although it is still clearly a significant improvement. The singly ionic (SIP) and doubly ionic (DIP) pairing models add successively smaller improvements.

Overall, the results in Tables 1 and 2 provide a useful quantification of the performance of the local correlation models discussed here for a simple but illustrative

model system. We hope to present additional calculations and studies that further characterize these methods in due course, as well as algorithmic developments that permit efficient implementation.

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