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Reducing the Computational Complexity of Electron Correlation Techniques:
Final Phase I SBIR Report to AFOSR

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Contents.

1. Summary of Achievements.

Quantitative prediction of the structure, properties, and chemical reactivity of molecules by computer programs using first principles electronic structure methods is a valuable complement to experimental studies, because the latter are often difficult or impossible for transient reactive species. Unfortunately, the electronic structure methods which achieve quantitative chemical accuracy, such as those based on coupled cluster theory, are currently limited in applicability to small molecules of less than about ten first row atoms. This is because of the unphysical increase in computational cost with molecular size in standard implementations. In this Phase I SBIR research, Q-Chem Inc., in collaboration with researchers at the University of California, Berkeley, has developed a new-from-the-ground-up approach to reformulating these proven electron correlation methods in terms of atom-centered spatially localized quantities. The feasibility and formal advantages of the new formulation has been demonstrated in preliminary work based on the simplest electron correlation method, second order perturbation theory. Trial calculations on medium sized molecules indicated that recovery of both absolute electron correlation energy, and also recovery of relative energies across potential surfaces is excellent. The results have shown the potential of these new local correlation methods to allow the study of much larger molecules than can be treated conventionally, with roughly an order of magnitude improvement being possible.

2. Introduction.

The main achievement of researchers in quantum chemistry over the past three decades has been the development of a rational series of theories of molecular wavefunctions which form successively better approximations to formally exact quantum mechanics[i]. Each approximation may be viewed as a "theoretical model chemistry", in the sense that virtually any property of the isolated molecule which can be measured experimentally can be calculated within the chosen framework. The goal of quantum chemistry is the achievement of model chemistries which are sufficiently accurate to permit prediction of molecular structure, properties and reactivity in cases where experiments are ambiguous or unfeasible. This can now be considered virtually accomplished for small molecules[ii,iii].

As a result of this systematic development, molecular orbital methods have been implemented into large program packages which have been eagerly adopted by researchers in industry and academia alike. There are now roughly ten major software packages which are competing for sales in this growing market. Applications of these methods range from investigating the thermochemical stability of chlorofluorocarbon replacements to calculations of the partial charges on small biological molecules as input to simulations for computer-aided drug design. Within the USA, molecular orbital calculations are used as a tool within most industrial molecular modeling groups. Part of maintaining their international competitiveness is to ensure that such groups have the earliest possible access to new technical advances, as has historically been the case in this area.

Yet this success masks an absolutely fundamental problem, which must be addressed if these model chemistries are ever to be applied to molecules containing more than a dozen or so atoms. The problem is that the computational complexity of our best model chemistries (for example based on the Møller-Plesset and coupled cluster approaches) grows in an *unphysical way* with the number of atoms. While electrons interact in pairwise fashion, the complexity of the coupled cluster approach to electron correlation rises as the sixth power of the size of the molecule[iv]. This is so steep a dependence that to increase the size of molecule by a factor of 10 would require *one million times* more computing power with present algorithms! Even computer storage requirements currently rise as the fourth power of molecular size, so ten thousand times more disk space would also be required.

One way around this barrier to the study of larger systems by molecular orbital methods is to seek entirely new theories. For this reason, much attention has been focused on density functional theory (DFT) over the past several years. Density functional methods scale far less severely with molecular size, and recover the proper asymptotic quadratic size dependence expected from pairwise interactions[v]. DFT is now widely employed for quantum mechanical calculations on large molecules. However, the accuracy of DFT is all too often insufficient for chemical purposes. For example, barriers to chemical reactions, which are critical in many molecular design applications, are predicted erratically by present versions of DFT. Hence DFT methods are not proving to be a replacement for accurate Møller-Plesset and coupled cluster theory calculations, which remain the methods of choice for quantitative calculations when they are computationally feasible.

The other alternative, which is the one that we have pursued in this research, is to *reformulate* high level molecular orbital theories to make them computationally feasible for studying larger molecules. The correlations between electrons must simplify as the separation between them increases, so that asymptotically it should be possible to obtain computational complexity that increases only with the *square* of molecular size, corresponding to pairwise interactions. The length scale on which this simplification occurs can be estimated very roughly from the length scale over which the characteristic functional group properties of molecules emerge. This is on the order of only a few bondlengths, which suggests that for molecules containing more than a few functional groups there will be tremendous computational savings from exploiting the natural distance dependence of electron correlations.

We have developed a new-from-the ground-up tensor-based formulation of electron correlation during the Phase I period which opens the way to new and very powerful "atoms-in-molecules" (AIM) methods that indeed make high level correlation methods applicable to larger molecules. In Sec. 3, we describe the underlying basis of the tensor formulation, and summarize some of the key new results that have been obtained. Perhaps the most significant one is the fact that the tensor approach permits use of nonorthogonal atom-centered functions in theories of electron correlation. In Sec. 4, we describe two procedures we have developed for obtaining appropriate sets of atom-centered functions, together with preliminary results. As described in Sec. 5, we have combined these two developments to obtain computationally efficient AIM treatments of electron correlation. Any standard correlation method can be evaluated by our AIM models. We have demonstrated their accuracy and feasibility via a pilot implementation for the simplest electron correlation method, second order Møller-Plesset theory.

3. A Tensor Approach to Electron Correlation Theory.

In the Phase I period, we have developed a straightforward formalism that allows theories of electron correlation to be formulated in nonorthogonal basis sets[vi]. Our treatment makes full use of the tensor properties of the operators of quantum mechanics, which permits all defining equations to be cast in a manner which is manifestly invariant to whether or not the basis is orthogonalized. The only assumption required is strong orthogonality between functions spanning the occupied subspace and functions spanning the virtual subspace of the one-particle Hilbert space. Even this can be lifted by the introduction of projectors into the equations. The tensor approach is readily employed using algebraic methods in either first or second quantization. When applied to standard correlation methods, such as coupled cluster theory truncated at single and double substitutions, and second order Møller-Plesset perturbation theory we obtain equations which are invariant to larger classes of transformations than existing expressions.

What is the point of permitting the generalization to nonorthogonal functions? In the first instance it is desirable to obtain expressions for many-electron theories that are as general as possible. One might imagine that given such equations, new and useful practical approximations may subsequently arise. For example, the atomic orbital (AO) single particle basis sets ubiquitous in molecular electronic structure theory are themselves nonorthogonal. To obtain equations that are directly in terms of this given basis set, there is no alternative but to properly build nonorthogonality into the formalism from the outset. Since these functions are spatially localized, they provide a natural representation in which the description of electron correlation via many-body theories can be cast in local terms. A spatially localized treatment of electron correlation[vii,viii] is essential for eliminating the unphysical scaling of computational cost with molecular size that afflicts orthogonal basis formulations of many-body theories.

Why was a formulation of this kind not already available? All standard many body methods in electronic structure theory, be they first quantization-based, second quantization-based or diagrammatic, implicitly depend upon an underlying orthonormal single particle basis[ix]. The main reason for employing orthogonal representations is that they are widely believed to be simpler. In particular, the usual approach to obtaining equations that are directly in a nonorthogonal basis is to explicitly carry the metric (overlap) matrices along in the equations[x]. This leads to equations that are substantially more cumbersome in the nonorthogonal basis than in the usual orthogonal representation. However, with the full use of tensor algebra, we have shown it is possible to obtain expressions that are general to nonorthogonal basis sets with relatively little additional complication.

Space considerations prevent us from giving a full description of the tensor formalism here. Instead, we shall summarize the essential concepts, and then illustrate the form of the equations that arise for second order Møller-Plesset theory. The equations that arise for coupled cluster theory are also straightforwardly obtained, and will be explored and implemented as part of our Phase II research.

Descriptions of tensor analysis are available in many textbooks[xi,xii]. For our purposes the essential concepts are:

1) Let us be given a set of nonorthogonal functions, $\left\{\left|\phi_{\mu}\right\rangle\right\}$ The way in which these functions transform on a change of basis is termed covariant, and covariant indices are denoted with subscripts. The overlap matrix of these functions is termed the metric: $g_{\mu\nu} \equiv S_{\mu\nu}$.

2) By inverting the metric matrix (or employing a generalized inverse if necessary) and acting with this inverse, $g^{\mu\nu} \equiv \left(S^{-1}\right)_{\mu\nu}$, on the given functions, we define a dual basis,

$$\left\langle\phi^{\mu}\right| = \sum_{\nu} g^{\mu\nu}\left\langle\phi_{\nu}\right| \tag{1}$$

which is biorthogonal to the original functions: $\left\langle\phi^{\mu}\middle|\phi_{\nu}\right\rangle = \delta^{\mu}_{\bullet\nu}$. Functions in the dual basis transform in an inverse way to functions in the given, covariant basis, and indices with this property are termed contravariant, and are indexed with superscripts. The action of the metric matrix converts indices from contravariant to covariant, and the inverse metric matrix converts from covariant to contravariant.

3) By defining addition and contraction of tensors appropriately, tensor algebra yields results which are by construction invariant to transformations of the underlying basis. Thus contraction of a pair of indices (as in a dot product of vectors to yield a scalar) is permitted only if one index is contravariant and the other is covariant, which defines the Einstein summation convention (a repeated index, one covariant the other contravariant, implies summation). Addition of tensors is only possible if the properties of their indices match.

4) To treat the electron correlation problem, we introduce separate sets of nonorthogonal functions spanning the occupied and virtual subspaces. How they are obtained is discussed in Sec. 3.3. Use of what we term the "natural representation" in which many-electron ket quantities contain functions in the covariant basis, and many-electron bra vectors contain only dual basis functions leads to equations for electron correlation methods that are isomorphic to traditional orthogonal basis derivations, but substantially more general.

5) While the discussion above appears to involve explicit inversion of metric matrices, which appears to rule out the use of linearly dependent representations, this is not in fact the case. With appropriate use of the theory of generalized inverses[xiii], and the singular value decomposition, it is quite straightforward to employ overcomplete representations (as we in fact do in practice, as discussed in Secs. 4 and 5).

We give an example of the tensor formalism applied to perhaps the simplest useful treatment of electron correlation. This is the many-body perturbation approach first proposed by Møller and Plesset[xiv]. Revived in the mid-1970's, this approach, carried to second order, has become a standard tool of computational quantum chemistry[i]. The usual formulation of MP2 theory involves the assumption of the canonical molecular orbitals (so that the zero Hamiltonian is diagonal in the many-electron basis). However, more general "noncanonical" forms of MP2 theory which are invariant to unitary transformations within the occupied and virtual spaces were introduced in the context of gradient theory, and open shell problems[xv]. With Pulay and Saebø's local MP2 method[vii], a yet more general form was presented, in which nonorthogonal functions were employed to span the virtual function space. Our tensor formalism yields the most general MP2 equations yet presented, as they are invariant to nonunitary transformations within the occupied and virtual spaces individually.

There is a delightful isomorphism between our new and more general treatment and the conventional orthogonal basis formulations. The first order equation for the perturbed wavefunction may be resolved by projection with singly and doubly substituted bra determinants (in the dual basis of course) to yield equations for the first order single and double substitution amplitudes:

$$\left\langle \Phi_i^a \middle| F^{(0)} \middle| T_1^{(1)} \Phi \right\rangle + \left\langle \Phi_i^a \middle| \hat{V}^{(1)} \middle| \Phi \right\rangle = 0 \tag{2a}$$

$$\left\langle \Phi_{ij}^{ab} \middle| F^{(0)} \middle| T_2^{(1)} \Phi \right\rangle + \left\langle \Phi_{ij}^{ab} \middle| \hat{V}^{(1)} \middle| \Phi \right\rangle = 0 \tag{2b}$$

These equations may be written out in explicit spin-orbital notation quite easily, using either first quantization tensor-based techniques or the corresponding second quantization version. Adopting the natural representation defined above for all tensor quantities we obtain:

$$F_b^a t_i^b - F_i^j t_j^a + F_i^a = 0 \tag{3a}$$

$$F_c^b t_{ij}^{ac} + F_c^a t_{ij}^{cb} - F_j^k t_{ik}^{ab} - F_i^k t_{kj}^{ab} + \mathit{\Pi}_{ij}^{ab} = 0 \tag{3b}$$

where ***F*** is the Fock operator, ***t*** are the amplitudes to solve for, and indices *i,j,k...* are occupied, *a,b,c...* are virtual, and of course subscripts and superscripts have their tensorial meanings. The antisymmetrized two electron integrals are explicitly defined in the natural representation as:

$$\mathit{\Pi}_{rs}^{pq} = \left\langle \phi^p \phi^q \middle| \phi_r \phi_s \right\rangle - \left\langle \phi^p \phi^q \middle| \phi_s \phi_r \right\rangle \tag{4}$$

Finally, the second order expansion of the energy is obtained from the second order expansion of the eigenvalue equation followed by projection with the bra determinant:

$$E^{(2)} = \left\langle \Phi \middle| V^{(1)} \middle| \left(T_1^{(1)} + T_2^{(1)} \right) \Phi \right\rangle = F_a^i t_i^a + \tfrac{1}{4} \mathit{\Pi}_{ab}^{ij} t_{ij}^{ab} \tag{5}$$

These equations constitute the most general form of the MP2 equations yet presented: they are invariant to general nonunitary linear transformations within the occupied and virtual subspaces respectively. Within the framework for treating linear dependencies mentioned above, these equations can even be solved within redundant representations if this is convenient. These equations, despite their perturbational nature, must be solved iteratively because of the off-diagonal Fock terms in Eqs. (3). Finally, Eqs. (3) can be specialized to the textbook canonical case by assuming an orthogonal basis (in which case the covariant-contravariant distinction vanishes), satisfying the Brillouin theorem (such that first order singles are zero), and diagonalizing the occupied-occupied and virtual-virtual blocks of the Fock matrix (so that the doubles equations uncouple).

Via the use of metric matrices, it is straightforward to alter the tensor character of the integrals and amplitudes that enter the above equations. For example, let us make contact with the expressions previously presented for the MP2 equations in a representation where the virtual subspace was treated in a redundant nonorthogonal representation while the occupied subspace was described in a noncanonical but orthogonal basis[vii]. We must make essentially only one change, which is to convert to the fully covariant virtual representation via metric matrices. The result is then directly comparable with the equations that form the starting point for Pulay and Saebø's local MP2 method[vii]:

$$S_{ac}t_{ij}^{cd}F_{bd} + F_{ac}t_{ij}^{cd}S_{bd} - F_j^k S_{ac}t_{ik}^{cd}S_{bd} - F_i^k S_{ac}t_{kj}^{cd}S_{bd} + I\!I_{abij} = 0 \tag{6a}$$

$$E^{(2)} = \tfrac{1}{4} I\!I_{ab}^{ij} t_{ij}^{ab} \tag{6b}$$

In their local MP2 method, the occupied indices are restricted to an orthogonal basis, so that the metric matrices for the occupied space are simply identity matrices, and the distinction between covariant and contravariant occupied indices vanishes. They also truncate the range of virtual indices associated with a given pair of occupied indices using a spatial proximity condition[vii,xvi].

To summarize, we have equations for second order Møller-Plesset theory (MP2) and coupled cluster theory which are more general than any previously reported. These equations permit the use of local nonorthogonal functions to represent both occupied and virtual subspaces, by contrast with all previous formulations which have required orthogonality in at least the occupied subspace. Two principal issues must be addressed in order to begin to leverage the very exciting potential of this new formulation for reducing the computational complexity of electron correlation methods. They are:

(1) We must define effective techniques for obtaining spatially localized sets of functions that span the occupied and virtual subspaces. Our solutions to this problem are discussed in Sec. 4. This bypasses the need for sets of localized molecular orbitals, and the problems that are sometimes associated with them.

(2) We must design a rational hierarchy of local correlation models that can be implemented and tested with the functions developed above. This leads to our "atoms-in-molecules" (AIM) methods for treating electron correlation, described in Sec. 5, which turns out to have unique formal and practical advantages relative to previous proposals for local MP2 methods.

4. The Nonorthogonal Orbitals.

We have decided to focus on atom-centered functions, so that our new models for local correlation can be based on *atom-centered selection* of the significant pair correlation amplitudes. The use of atom-based functions is very common within single electron theories of electronic structure such as Hartree-Fock theory and density functional theory. In the context of the tensor-based electron correlation formalism developed in Sec. 3, we require sets of functions spanning the occupied and virtual subspaces. The most simple approach is to use projected atomic orbitals: projected into the occupied space and the virtual space respectively:

$$\left|\phi_i\right\rangle = \hat{P}\left|\phi_\mu\right\rangle\delta_i^\mu = \left|\phi_\mu\right\rangle P_{\bullet\nu}^{\mu}\delta_i^\nu \tag{7a}$$

$$\left|\phi_a\right\rangle = \hat{Q}\left|\phi_\mu\right\rangle\delta_a^\mu = \left(\hat{I} - \hat{P}\right)\left|\phi_\mu\right\rangle\delta_a^\mu = \left|\phi_\mu\right\rangle\left(\delta_a^\mu - P_{\bullet\nu}^{\mu}\delta_a^\nu\right) \tag{7b}$$

This leads to functions which for insulators are exponentially localized, provided the system under study has a band gap. This condition is universally satisfied for molecules. The use of functions of this type is satisfactory for the virtual space and has been used successfully in the earlier local correlation models of Pulay and Saebø[vii]. However projected atomic orbitals are several-fold redundant (and hence potentially inefficient) for the occupied space.

We have hence developed alternative treatments of the occupied space which reduce its dimension per atom to that of a minimum basis only (instead of the dimension of the full basis for correlation which will typically be 3 to 10 times larger). It has been long suspected that such a reduction is possible[xvii,xviii] with little loss in accuracy, but the idea has never been pursued for computational advantage. We have accomplished the reduction to a minimum basis in two alternative ways, which each have different special advantages. We shall discuss them in turn.

Projected Natural Atomic Orbitals (PNAO's). This is an *exact* reduction, based on defining natural atomic orbitals from atom-centered blocks of the one-particle density matrix, in the spirit of Weinhold's natural atomic orbitals[xix]. Selecting a minimum basis set according to occupation number and projecting into the occupied space (via the analog of Eq. (7a)) yields functions that exactly span that space.   for all molecules tested (an extensive series of compounds comprised of first row atoms and hydrogen atoms). This set of localized atom-centered functions gives a starting point for correlation treatments that is exactly equivalent to the conventional choice of a set of occupied molecular orbitals. The extent of localization is directly related to the bandwidth of the density matrix.

Projected Polarized atomic orbitals. We have developed an alternative reduction in which the Hartree-Fock calculation that defines the occupied space is performed in a *molecule-optimized atom-centered minimum basis set*. We term these functions *polarized atomic orbitals* (PAO's) and we have developed a pilot program that determines them as linear combinations of the functions included in a much larger secondary basis set. For example, the triple zeta 6-311G** basis is employed to define the molecule-optimized minimal basis of PAO's in the preliminary results discussed below. Thus given a (large) secondary basis $\{|\phi_\mu\rangle\}$, the (small) basis of PAO's $\{|\phi_\alpha\rangle\}$ are defined via an atom-blocked (let PAO index α belong to atom A) rectangular transformation, $\mathbf{B}$:

$$|\phi_\alpha\rangle = \sum_{\mu \in A} |\phi_\mu\rangle B_{\mu\alpha} \tag{8}$$

where the transformation coefficients are determined as part of the variational Hartree-Fock calculation.

The PAO's appear very promising as a method for performing HF (or even DFT) calculations on very large molecules as well as providing atom-centered functions that span the occupied space (after projection with the density operator). While the Hartree-Fock energy obtained in this way is slightly higher than that in the full (extended) basis, this difference is small compared to normal basis set incompleteness effects. More importantly, the quality of chemical results obtained with the PAO basis is vastly higher than that of a conventional minimal basis, and approaches that of the full secondary basis.

An example of the Phase I tests of PAO's are shown in Tables 1 and 2, which contains PAO Hartree-Fock and PAO second order Møller-Plesset theory calculations on a small series of substituted ethylenes, probing both the absolute energy of the most stable conformer (table 1), and the relative energies of the stable conformers and the transition state for internal rotation (table 2). *As these molecules are all conjugated, they represent a stringent test for the performance of the PAO model.* In particular, the PAO model of bonding approaches exactness in the limit where all bonds are strictly localized. This is clearly not the case in these conjugated molecules, where the size of the rotational barrier follows directly from the strength of the conjugative interactions between the two unsaturated groups.

conformation	HF/ PAO[6-311G**]	HF/ 6-311G**	MP2/ PAO[6-311G**]	MP2/ 6-311G**
Vi-CHO (trans)	-190.775497	-190.812472	-191.497914	-191.504270
Vi-OH (trans)	-152.904239	-152.937832	-153.473099	-153.477798
Vi-Vi (trans)	-154.929678	-154.960122	-155.592566	-155.595937
Vi-CFO (trans)	-289.656809	-289.718733	-290.600770	-290.612309

Table 1. Hartree-Fock and second order Møller-Plesset calculations of the absolute energies of the most stable conformer of a series of conjugated ethylenes: acrolein (Vi-CHO), vinyl alcohol (Vi-OH), butadiene (Vi-Vi), and propenoyl fluoride (Vi-CFO). All calculations are at HF/6-31G* optimized geometries and the absolute energies are given in atomic units (Hartrees). Differences between using the polarized atomic orbitals, and full use of the 6-311G** basis are smaller than the basis set truncation errors. Furthermore, this difference is greatly reduced, by a factor of 4 to 10, at the MP2 level.

conformation	HF/ PAO[6-311G**]	HF/ 6-311G**	MP2/ PAO[6-311G**]	MP2/ 6-311G**
Vi-CHO (trans)	0.0	0.0	0.0	0.0

Vi-CHO (cis)	2.162	1.688	1.610	1.450
Vi-CHO (t.s.)	6.649	7.954	7.691	7.874
Vi-OH (syn)	0.0	0.0	0.0	0.0
Vi-OH (anti)	2.777	1.992	2.131	2.051
Vi-OH (t.s.)	4.352	4.574	5.978	5.573
Vi-Vi (trans)	0.0	0.0	0.0	0.0
Vi-Vi (gauche)	3.199	3.178	2.730	2.652
Vi-Vi (cis t.s.)	4.038	4.098	3.731	3.699
Vi-Vi (perp. t.s.)	5.755	6.058	5.978	5.770
Vi-CFO (trans)	0.0	0.0	0.0	0.0
Vi-CFO (cis)	0.440	0.198	0.217	0.093
Vi-CFO (t.s.)	6.244	7.604	6.591	6.674

Table 2. Hartree-Fock and second order Møller-Plesset calculations of the relative energies of the stable conformations, and transition states for internal rotation, of the same series of substituted ethylenes given in table1. All calculations are at HF/6-31G* optimized geometries. Relative energies are given in kcal/mol. Differences between the use of PAO's and full use of the secondary basis leads to changes in barrier heights which are generally less than the estimated uncertainty of +/- 1 kcal/mol at the full MP2/6-311G** level[xx].

First let us consider the results in table 1 briefly. It is evident that the difference between PAO and full energies using 6-311G** as the secondary basis is only the order of several tens of milliHartrees. By comparison the total energy obtained in a true minimum basis (STO-3G) is over 2.5 Hartrees higher, for acrolein as a typical example! The PAO calculation allows us to quite closely approach the exact energy at this level of theory. Turning to the HF values of relative energies shown in table 2, we see that the difference between PAO relative energies at the HF level, and results obtained with the full 6-311G** basis are in general less than 1 kcal/mol. This is a difference which is significantly smaller than the estimated errors in the calculation! It is also far smaller than the energy differences between the PAO calculations and the full 6-311G** calculations, which is on the order of 20 kcal/mol. Almost entirely all of this difference is evidently common to the various isomers.

Let us now consider the similarities and differences between PAO results at the Hartree-Fock level of theory, and PAO results at the correlated MP2 level. Inspection of the results in tables 1 and 2 suggests the following main points:

1) From table 1, the difference between the total MP2 energy in the secondary basis, and the PAO-MP2 energy is *lower by a large factor* (between 4 and 10) than the corresponding Hartree-Fock differences. We have found this to be a general result, which is a consequence of the singles contribution to the MP2 energy corresponding to an energy-weighted steepest descent relaxation of the density matrix obtained in the PAO basis towards its true values.

2) As a result of this, the PAO-MP2 rotational energy barriers approach the full MP2 rotational barriers somewhat more closely than the PAO Hartree-Fock barriers approached the full Hartree-Fock barriers, as shown in table 2. The differences between PAO MP2 relative energies and relative energies calculated directly in the secondary basis is less than the estimated uncertainty of about +/- 1 kcal/mol in the full MP2 calculations[xx].

3) The corresponding differences between a PAO-HF reference and a full HF reference in an even better correlation treatment, such as coupled cluster theory, will be smaller by at least another equal factor, as such methods can easily compensate for the relatively small difference between the PAO HF reference, and the full HF reference in the basis used for the correlation treatment.

The use of PAO's offers enormous efficiency advantages for the treatment of electron correlation at the second order Møller-Plesset theory level. This advantage derives from the fact that occupied MO's can be directly represented in terms of unprojected PAO's, which constitute only a minimal basis. Having illustrated that the PAO model is chemically effective, we shall develop the sophisticated numerical methods necessary to exploit these advantages in Phase II. The availability of the alternative projected atomic orbital approach ensures that we can also offer the exact solution in the secondary basis.

5. Atoms-in-Molecules (AIM) Methods for Electron Correlation.

The developments described in the previous two sections constitute a formally exact re-expression of standard theories of electron correlation. In the traditional formulation, the nonredundant canonical molecular orbitals are employed to express many-electron theories. The canonical MO's are in general fully delocalized throughout the system. In our re-expression of electron correlation theories, redundant sets of atom-centered functions are used to develop the working equations. The question addressed in this section is how we exploit the spatial localization of these atom-centered functions to develop new local correlation models that involve drastically reduced computational complexity. The validity of strong local truncations was first demonstrated by Pulay[xxi]. *Our tensor-based formalism will permit comparable models to be formulated directly in terms of atom-centered truncations*, with significant formal and practical advantages.

First we discuss a completely general procedure for solving the MP2 equations in a subspace of the full four-index set of pair correlations. Let us initially make the two-electron integrals in the fully covariant representation, $I\!I_{ijab}$.

(1) *Definition of the truncated four-index ket space.* We discard a large number of the fully covariant integrals based on the models described below, leaving us with a reduced set in which the indices a,b,i,j are no longer independent. Instead we can view the retained *abij* as defining a single linear index, *(abij).* In tensor terms, this truncation has reduced the rank of the four index space from 4 to 1. Effectively we have selected a subset of the $\left|\Phi(ijab)\right\rangle$ within which we shall satisfy the equations. We will surround the compound index with brackets to indicate that the individual indices are no longer independent.

(2) *The definition of the metric of the truncated four-index space.* Have admitted that in the truncated space, we can no longer permit the indices a,b,i,j to be independent, we can no longer define the dual 4 index space in terms of simple products of the inverses of the single index metrics. For example, simply defining the dual space of truncated bra functions in that manner will lead to local correlation models in which the correlation equations are not solved in a well-defined subspace. Instead we first properly define the metric associated with our truncated ket space. This takes the general form:

$$G_{(ijab)(klcd)} = g_{ik}g_{jl}g_{ac}g_{bd} \tag{9}$$

If we need to transform a truncated tensor of character $t_{(ijab)}$ into character $t^{(klcd)}$ then the metric, (9), must be inverted either implicitly or explicitly:

$$G^{(klcd)(ijab)}t_{(ijab)} = t^{(klcd)} \tag{10}$$

(3) *Solution of the truncated equations.* We wish to solve the tensor MP2 equations within the subspace selected in Step (1) above, with metric characterized in Step (2). This leads us to the following explicit form of the truncated equations, in terms of the corresponding set of truncated amplitudes:

$$\left\{\left[F_{ac}g_{bd}+g_{ac}F_{bd}\right]g_{ik}g_{jl}-g_{ac}g_{bd}\left[F_{ik}g_{jl}+g_{ik}F_{jl}\right]\right\}t^{(klcd)} = -I\!I_{(ijab)} \tag{11}$$

This set of equations explicitly defines the form of the coefficient matrix in the truncated 4-index space. The equations can be solved by standard conjugate gradient or DIIS[xxii] techniques, although we note that as written here, the form of the residual on each iteration is not tensorially consistent with the form of the amplitudes that we must update. Conversion is accomplished via solution of Eqs. (10) (which need not be exact for this purpose). Finally, given the converged amplitudes in the truncated space, we obtain the MP2 energy in the form:

$$E^{(2)} = \tfrac{1}{4}t^{(ijab)}I\!I_{(ijab)} \tag{12}$$

When the correlation equations are solved in a truncated 4-index space in the above manner, we achieve solution of the equations within a well-defined subspace of the full set of double excitations. By contrast, if we did not employ the proper metric associated with the truncated rank 1, 4 index space, then the solution lacks this important model property. Hence our new methods are rigorously invariant to linear transformations that mix the retained excitations.

Within the Phase I project, we have formulated a series of truncations that are increasingly accurate. Since the truncations are based on our atom-centered functions spanning occupied and virtual spaces, we refer to these as "Atoms in Molecules" (AIM) models of localized electron correlation effects. We restrict the admissible correlation amplitudes, $t^{(ijab)}$, via the following models. We note that models such as these are entirely new, because they could not be constructed without the new developments described in Secs. 3 and 4.

(1) *Covalent two-center truncation*[xxiii]. Compound indices *(abij)* are retained if:

- indices *i* and *a* belong to the same center, and *j* and *b* belong to the same center. These interactions correspond to direct dispersion interactions at long range, and decay as inverse cube of length with the separation of the sites (assuming local neutrality).
- indices *i* and *b* belong to the same center, and *j* and *a* belong to the same center. These are the exchange interactions that complement the direct correlation effects above, ensuring a balanced approximation. These interactions (in insulators) decay exponentially with the separation of the separation of the sites, and thus for large molecules (in the range of tens of atoms) it becomes profitable to apply cutoffs to these terms. This model is in a sense the AIM analog of the original Pulay and Saebø proposal for a local ansatz[vii].

(2) *Full two-center model.* The most sophisticated two-center model is to retain all compound indices where no more than two centers are involved in all four indices. Only the dispersion-like interactions (identified in model (1)) are truly long-range, and thus cutoffs can be profitably applied to the model approximation. This model is exact for correlation of bond orbitals that are strongly localized.

The covalent two-center model can be shown to have several very beautiful formal properties which make it particularly attractive as a target theory. In particular, we have shown that:

(1) The metric is a *separable product* (because of its diatomic nature). This means that iterating to invert the full metric is not necessary. Instead we have explicitly inverted the mono-atomic metric via a singular value decomposition, and then formed the inverse of the diatomic metric as a tensor product. This entirely eliminates the necessity to solve Eq. (10), which is the first iterative step in the general local scheme described above.

(2) It is possible to recanonicalize the MP2 equations, (11), by exploiting the product nature of the metric. In particular the coefficient matrix that defines Eq. (11) separates into the sum of two products of lower rank matrices, one of which is the fundamental mono-atomic metric matrix, and the other of which is a mono-atomic excitation-like matrix. The former we have already diagonalized in the first step above. The latter can be diagonalized in the basis of eigenvectors of the metric, which makes the full MP2 coefficient matrix diagonal. As a result, *the AIM-MP2 method is entirely noniterative*, just

like conventional MP2, and entirely unlike previous local MP2 methods. The computational requirements for these two diagonalization steps are strictly cubic with the size of the molecule.

As is evident from the description above, there are tremendous practical advantages to employing the first AIM-MP2 model, as it can be made entirely noniterative. Therefore we have carefully investigated its behavior with respect to recovery of the exact MP2 correlation energy to see if it is a suitable model for practical chemical calculations. For the preliminary investigations completed in this Phase I work, we employed projected atomic orbitals for both occupied and virtual subspaces to permit direct comparison with conventional canonical MP2 calculations. A pilot code was developed which was not in any way optimized, hence we cannot report elapsed times at this stage. Rather the purpose of these calculations is to assess the quality of the chemical information that the new AIM models are capable of yielding. We know from straightforward numerical analysis of the new models that they are capable of being applied to very large systems, but achieving that goal is only worthwhile once it has been established that the results are of sufficient quality to be useful.

Tables 3 and 4 below summarize the results of a series of test calculations we have performed on conjugated molecules similar to those used to test the polarized atomic orbital model in Sec. 4. Table 3 reports the recovery of the absolute MP2 correlation energy, and it is evident that AIM-MP2 is capable of yielding roughly 99.9% of the correlation energy for these systems. This is a very high fractional recovery of the electron correlation energy, which is sufficiently good that we should expect the recovery of relative correlation energies to be excellent also. We note parenthetically that the problem of relative correlation energies is much tougher than absolute correlation energies because we are concerned with small energy differences (perhaps on the order of kcal/mol) between quite large correlation energies (on the order of Hartrees, or between 100 and 1000 kcal/mol). To obtain less than 10% error in a relative energy of that magnitude requires a differential error of less than about 0.03% between the points of interest on the potential surface, which is challenging indeed.

molecule	E(HF)/a.u.	dE(MP2)/a.u.	dE(AIM-MP2)	% correlation
Vi-C2H3	-154.960121	-0.560776	-0.560541	99.96
Vi-CFO	-289.718733	-0.799584	-0.799553	99.99
Vi-CHO	-190.812152	-0.604500	-0.604461	99.99
Vi-NH2	-133.103964	-0.466910	-0.466784	99.97
Vi-NO2	-281.578165	-0.853139	-0.853124	99.99
Vi-OH	-152.937831	-0.483513	-0.483439	99.98

Ph-CHO	-343.511145	-1.140552	-1.138509	99.82
Ph_NH2	-85.800480	-1.002452	-1.000878	99.84
Ph-OH	-305.634634	-1.017709	-1.016479	99.88

Table 3. Recovery of the canonical MP2 correlation energy by the local AIM-MP2 method. Calculations are using the 6-311G** basis set, at the lowest energy conformation of each molecule, which was optimized at the HF/6-31G* level. The final column is the percentage of exact correlation energy recovered by the AIM-MP2 model, which is typically in the vicinity of 99.9%.

molecule	Δ(HF)/kcal mol^{-1}	Δ(MP2)/kcal mol^{-1}	Δ(AIM-MP2)
Vi-C2H3	6.058061	0.313	0.270
Vi-CFO	7.604045	0.955	0.960
Vi-CHO	8.006900	0.106	0.109
Vi-NH2	6.477682	0.745	0.789
Vi-NO2	6.955837	1.834	1.787
Vi-OH	4.573220	0.975	0.958
Ph-CHO	8.809472	0.527	0.722
Ph-NH2	3.746802	0.510	0.665
Ph-OH	2.570867	0.788	0.723

Table 4. Differential recovery of the canonical MP2 correlation energy contribution to rotational energy barriers by the local AIM-MP2 method. Calculations are performed using the 6-311G** basis set, at geometries which were optimized at the HF/6-31G* level. All energies are reported in units of kcal/mol. It is evident that the AIM-MP2 method recovers these very small energy differences with errors of less than 10%. As discussed in the text, it is not clear that these errors are to be regarded as deficiencies relative to experiment.

Table 4 contains the results of relative correlation energy calculations for the rotational barriers in the conjugated molecules. It is clear that AIM-MP2 recovers the exact results to quite acceptable accuracy. On formal grounds, we expect these deviations to generally decrease as the basis set is further improved. Furthermore, on formal grounds it is not obvious that the "exact" results are to be preferred. As has been illustrated previously by Pulay and co-workers for the water dimer, and Friesner and co-workers for conformational energy differences in their local method, basis set superposition error

(BSSE) affects the exact results far more. The principal conclusion we draw from tables 3 and 4 is that the quality of our simplest AIM model is sufficiently high that we are able to exploit its desirable properties, and we are not forced at present to pursue the most general 4 center local model. This is pleasing both on physical grounds (for the model is simpler), and on practical grounds (the model is much faster and more efficient).

6. Epilog.

With the new Atoms-in-Molecules (AIM) approach for reducing the complexity of electron correlation methods in hand, the stage is set for the Phase II effort. This is the extension and efficient implementation of AIM methods for the highest level electron correlation treatments in routine use for small molecules: coupled cluster theory. The result will be a unique computational tool that permits routine, highly accurate treatment of problems that are in the range of an order of magnitude larger than is possible at present, using methods whose accuracy is already accepted and established beyond doubt!

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