Pseudospectral localized Møller−Plesset methods: Theory and calculation of conformational energies

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We have developed an algorithm based upon pseudospectral ab initio electronic structure methods for evaluating correlation energies via the localized Møller−Plesset methodology of Pulay and Saebo. Even for small molecules (~ 20 atoms) CPU times are diminished by a factor of ~ 10 compared to canonical MP2 timings for Gaussian 92 and the scaling is reduced from $N^4 - N^5$ in conventional methods to $\sim N^3$. We have tested the accuracy of the method by calculating conformational energy differences for 36 small molecules for which experimental data exists, using the Dunning cc-pVTZ correlation consistent basis set. After removing 6 test cases on the grounds of unreliability of the experimental data, an average deviation with experiment of 0.18 kcal/mol between theory and experiment is obtained, with a maximum deviation of ~ 0.55 kcal/mol. This performance is significantly better than that obtained previously with a smaller basis set via canonical MP2; it is also superior to the results of gradient corrected density functional theory. © *1995 American Institute of Physics.*

I. INTRODUCTION

Second order Møller−Plesset perturbation theory (MP2) is one of the core techniques in ab initio electronic structure theory. It is the least expensive wave function based (as opposed to density functional (DF)) method in which a substantial fraction of the correlation energy is recovered. While DF methods have made remarkable progress over the past 5 years, yielding atomization energies for small molecules that are superior to MP2,[1] there are still difficulties in calculating dispersion interactions, hydrogen bonds, and other weak forces with DF methods. MP2, in contrast, is believed to be rather reliable for such problems provided a sufficiently large basis set is used. Finally, in conjunction with a multiconfigurational reference [e.g. GVB,[2] GVB-RCI Ref. 3,) a series of papers from the groups of Pulay,[4,5] Roos,[6,7] and Messmer[8,9] have shown that near-chemical accuracy can be obtained by correcting these MC-SCF wavefunctions with the multiconfigurational analog of the MP2 methodology. As we have recently demonstrated[3] a high quality MCSCF methodology (GVB-RCI) which scales as N^3 (where N is the basis set size), the development of a similarly efficient MP2 algorithm would allow highly accurate calculations on very large molecules, e.g. in the 50–100 atom range.

In the present paper, we demonstrate that by using pseudospectral numerical techniques in combination with the localized formulation of Pulay and Saebo,[10] an MP2 algorithm that scales as N^3 (more specifically, n^2N, where n is the number of occupied orbitals) while retaining traditional accuracy of conventional electronic structure codes can be devised. For a calculation using a DZP basis with 250 functions, the method is already five times more efficient than the MP2 code in GAUSSIAN 92.[13] Extrapolations of the timing results presented below to the 1000 basis function limit indicate that our PS-LMP2 method is approximately 25 times faster than GAUSSIAN 92 for a 6-31G** basis and 250 times faster for a TZP basis such as the Dunning cc-pVTZ (Ref. 14) correlation consistent basis. This means that new areas of chemistry are opened up to MP2 (and GVB-RCI-MP2) methods by the present approach.

The key to the improved scaling is that the two electron integrals which go into the MP2 energy expression can be calculated directly over molecular orbitals in the PS method, avoiding the traditional four index transform of standard methods. For canonical MP2, this does not gain anything because there are n^2N^2 integrals to evaluate and each integral requires N_{grid} operations to calculate, leading to a $\sim N^5$ scaling that is identical to that obtained in the usual analytical integral technology. However, in the localized formulation of MP2, there are instead $n^2N_v^2$ integrals to evaluate, where N_v is a fixed virtual space size that does not change as the molecule grows larger. This removes two powers of N and leads to N^3 scaling as asserted above.

The LMP2 energies will not, of course, agree exactly with canonical MP2, although the difference in correlation energy is small, typically on the order of 1%. Pulay and Saebo have argued that[11] LMP2 energies differences are superior to canonical MP2 as one would expect significantly fewer problems with basis set superposition error (BSSE). Saebo and Pulay provided a practical demonstration of this point in an extensive series of calculations on the water dimer.[12] In that paper, it was shown that LMP2 rapidly converges to a result very close to experiment for the water dimer binding energies, while canonical MP2 is on the order of 0.5 kcal/mol off this value for rather large basis sets and converges to the correct result only when enormous basis sets are utilized. Furthermore, the so-called counterpoise correction overcompensated for the BSSE, leading to a result

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that was equally inaccurate in the opposite direction.

Recently, St. Amant *et al.*[15] have assembled a data base of 36 molecules from the literature for which experimental evaluation of gas phase conformational energy differences are available. They calculated these energy differences via canonical MP2 using a TZP basis set and with gradient-corrected DFT methods. While the results were in many cases in agreement with experiment for both approaches, each method had a significant subset of molecules for which substantial errors were obtained. Indeed, the average errors per molecule (0.35 kcal/mol for both MP2 and DFT) was a marginal, if definite, improvement over the Hartree–Fock results (average error 0.52 kcal/mol).

In the present paper, we carry out LMP2 calculations on this same test set of 36 molecules to test the accuracy of LMP2 methods. We utilize the Dunning cc-pVTZ correlation consistent basis[14] rather than the older Dunning TZP basis employed in Ref. 15; this eliminates many of the serious discrepancies with experiment that were attributed to the MP2 method in Ref. 15. When canonical MP2 and LMP2 are compared for the same basis set, the results are typically within ~ 0.3 kcal/mol, indicating that BSSE problems are minimal for most of the cases studied here.

The paper is organized as follows. In section II, we review the theory of LMP2, while in section III, we describe the PS LMP2 algorithm in detail. In section IV, we present our conformational energy calculation and discuss the results in depth. In section V, we carry out timing comparisons, not only with Gaussian 92 canonical MP2 but also with DFT calculations. Finally, in section VI, the conclusion, we discuss future development of LMP methods (e.g. LMP3, GVB-LMP) and expected improvements in performance of our code over the next year.

II. LOCALIZED MP2 METHODS

The basic idea of LMP2 is extremely simple. It is based upon the fact that for virtually all molecules, one can construct a localized orbital representation of the occupied space that is equivalent to the usual Hartree–Fock canonical orbitals which are typically delocalized over the entire molecule. One way to do this is to employ Boys localization,[16] a unitary transformation of the canonical orbitals designed to optimize localization. Alternatively, GVB methods generate localized orbitals automatically in the course of the MCSCF iteration process.

The typical result of Boys or GVB localization is that each orbital has substantial amplitude on one atom (lone pair) or two atoms (bond). This localization procedure works even for cases like benzene, yielding orbitals for that molecule appropriate to one set of Kekule structures. Remarkably, as is shown below, the LMP2 energy differences for benzene are in quite good agreement with conventional MP2 results, and in terms of energetics, there are no problems with symmetry (one might run into a problem trying to calculate wavefunction properties such as the quadrupole moment with LMP2, however). There may well be some cases, such as s electrons in metals, where the localization procedure breaks down; however, we have not investigated this type of system in the present paper.

Following Pulay and Saebo,[10] we expand the first order wavefunction in a basis of determinants in which the virtual orbitals are nonorthogonal, and are dependent upon the occupied orbitals from which excitation takes place. The first order correction $\Psi^{(1)}$ to the Hartree–Fock reference is:

$$\Psi^{(1)} = \sum_{i \geqslant j} \sum_{p,q} C_{ij}^{pq} \Psi_{ij}^{pq}, \tag{1}$$

with Ψ_{ij}^{pq} denoting a doubly substituted generator state function made by exciting from ij occupied, localized orbitals to pq localized virtual orbitals. In canonical MP2 theory, the coefficients C_{ij}^{pq} are simplified by the fact that the orbitals are eigenfunctions of H_0, the Fock operator,

$$C_{ij}^{pq}(\text{canonical}) = \frac{K_{ij}^{pq}}{\epsilon_i + \epsilon_j - \epsilon_p - \epsilon_q}, \tag{2}$$

where K_{ij}^{pq} is the exchange integral,

$$K_{ij}^{pq} = \int \frac{p(r_1)i(r_1)q(r_2)j(r_2)}{r_{12}} \, dr_{12} = (pi|jq), \tag{3}$$

and ϵ_i are canonical orbital eigenvalues. In LMP2, however, one has to solve an iterative equation, obtained from the Hylleras variational form of the second order energy. This equation has been derived in detail by Pulay and Saebo[11] and we shall not repeat this here; the equation is:

$$\mathbf{T}_{ij}^{(2)} = \mathbf{K}_{ij} + \mathbf{F}\mathbf{C}_{ij}\mathbf{S} + \mathbf{S}\mathbf{C}_{ij}\mathbf{F} - \mathbf{S}\sum_k \ [F_{ik}\mathbf{C}_{kj} + F_{kj}\mathbf{C}_{ik}]\mathbf{S}$$

$$= 0, \tag{4}$$

where $\mathbf{F}$ is the Fock matrix and $\mathbf{S}$ is the overlap matrix. Matrices such as $\mathbf{K}_{ij}$ are restricted to the dimensions of the virtual space for the occupied pair ij. The second order energy correction $E^{(2)}$ is simply

$$E^{(2)} = \sum_{i \geqslant j} \langle \mathbf{K}_{ij}\tilde{\mathbf{C}}_{ji} \rangle; \quad \tilde{\mathbf{C}}_{ji} = (1 + \delta_{ij})^{-1}(4\mathbf{C}_{ij} - 2\mathbf{C}_{ji}) \tag{5}$$

with the bracket denoting a trace.

The use of localized occupied orbitals and nonorthogonal virtual orbitals leads to off-diagonal terms in the Fock operator and overlap matrix above, which prevent the analytical solution of Eq. (4) as is straightforward in canonical MP2 theory. However, the iterative equations converge in a small number of iterations and have a reasonable prefactor and scaling with system size, as shown below. Consequently, they present no barrier to the efficient use of LMP2 methods.

For larger basis sets such as cc-pVTZ we have found that to obtain a stable solution of Eq. (5) it is necessary to effectively remove high energy virtual orbitals which have a very large coefficients in their AO expansion. The large coefficients of these virtuals create an instability since the square of these coefficients in the formation of K_{ij}^{pq} greatly magnifies any pseudospectral error in the integral. The automated procedure in our code for this removal involves defining the virtuals to be orthogonalized to as those which have a sum of their AO coefficients which is more than twice the average coefficient sum for the virtuals. The remaining vir-

tual orbitals are then orthogonalized to this selected set. This procedure is completely automatic and does not require adjustment on a case by case basis. Furthermore, since the local virtual space itself is not complete, this procedure does not cause any incompleteness in the pair virtual space. For the test cases studied here only about 10% of the molecules required removal of from one to three virtuals. The fact that accurate conformational energy differences were obtained for the cases with virtual orbitals removed suggests that this procedure for removing high energy virtuals is stable.

The formulation above is a powerful one because it allows the use of any occupied orbitals (as long as they are obtained from a unitary transformation of the canonical orbitals) and any virtual space. The basic physical idea is then that correlation is local and a local basis should be sufficient to correlate each localized orbital. We follow the prescription of Pulay and Saebo in which the virtual space for a pair excitation ij is taken to be the atomic basis functions on the atoms on which i and j have large coefficients, orthogonalized to the occupied space. The last of these procedures means that the correlating orbitals are not particularly well localized in space, an observation that has impeded efforts to use cutoffs in conventional implementations of LMP2. However, in the PS implementation, spatial localization of the virtual orbitals is unneccessary to achieve huge gains in computational efficiency. The key is in the reduction of the number of virtual orbitals for each occupied pair to a fixed value, independent of system size. Note that in this initial implementation all occupied valence pairs ij are correlated. Future implementations will allow for weakly correlated pairs to be left uncorrelated.

For excitation of a pair of electrons from two localized chemical bonds, a maximum of four atoms, two atoms from each bond, will contribute to the set of virtual functions correlating the ij bond pair. For a DZP basis and four first row heavy atoms, this leads to a total size of the virtual space of order 60 functions per bond pair . Larger basis sets, e.g. TZP, will of course result in a larger virtual space; however, this will have no effect on the scaling of the calculations with system size for a given basis type.

III. PSEUDOSPECTRAL MP2 METHODS

A. Analysis of conventional four index transform methods

The expressions for the canonical MP2 second order energy correction and the local MP2 correction in Eq. (5) require the exchange integrals K_{ij}^{pq} involving two occupied and two virtual orbitals. In conventional electronic structure codes, K_{ij}^{pq} is evaluated by a four-index transformation of the AO integrals K_{mn}^{kl} to the requisite orbital space. In conventional electronic structure codes this transformation is evaluated by carrying out the sum one index at a time. Thus, the first step in the four index transform takes a linear combination of exchange integrals [Eq. (3)] K_{mn}^{kl} with $klmn$ in the AO basis,

$$K_{il}^{mn} = \sum_k c_{ki} K_{kl}^{mn} = \sum_k c_{ki}(mk|nl), \tag{6}$$

and c_{ki} the coefficient of orbital i in the AO basis. The second step is then

$$K_{ij}^{mn} = \sum_l c_{lj} K_{il}^{mn}, \tag{7}$$

and so on until all of the indices refer to molecular orbitals. Note that the first steps in the transforms above contain no reference to virtual orbitals, and are thus entirely unaffected by the use of the localized MP2 formalism. Only steps 3 and 4 are impacted, with the greatest impact being on step 4.

It is possible in principle to reduce the scaling of steps 1 and 2 by the use of cutoffs. However, these cutoffs are much less efficacious than in the corresponding usage in Hartree–Fock theory. The reason is that the major expense in a direct SCF calculation is the computation of two electron integrals. This depends strongly on the degree of contraction in the basis set. The integral cutoffs are very effective at throwing out contracted primitives with large exponents, thus drastically reducing the degree of contraction. This leads to substantial CPU reductions for two electron integral calculation.

However, to be of use in reducing operation counts for the four index transform, it is necessary to discard the entire integral. This is much less likely than discarding a contracted primitive quartet as it is dependent upon having small overlaps between primitives containing the smallest exponents in each basis function; the large gains obtained by integral cutoffs in GAUSSIAN 92 arise from substantial reductions in the terms proportional to K^4, where K is the effective contraction degree. While the actual effectiveness that can be obtained can be determined only by empirical experimentation, it is clear from examination of typical basis sets that very large molecules will be required before the scaling can be reduced to the theoretical limit of N^3. This analysis is confirmed by the results reported below for GAUSSIAN 92, in which integral cutoffs are implemented. Of course, future improvements in the conventional MP2 algorithms may yield better performance.

B. Pseudospectral formulation

1. Basic theory

In localized pseudospectral MP2, the key step is generation of the two electron integrals over the occupied and virtual local MOs. These are formed directly from the following sum over grid points g,[17]

$$K_{ij}^{pq} = \sum_g Q_i(g) R_p(g) A_{jq}(g). \tag{8}$$

Here Q_i is the least squares fitting operator for molecular orbital i, R_p is the physical space representation of virtual orbital p, and $A_{jq}(g)$ is the three center, one electron integral over molecular orbitals j and q given by

$$A_{jq}(g) = \sum_{kl} c_{kj} c_{lq} A_{kl}(g)$$

$$= \sum_{kl} c_{kj} c_{lq} \int \frac{\chi_k(1)\chi_l(1)}{r_{1g}} d\mathbf{r}_1 \tag{9}$$

with $\chi_{k,l}$ denoting contracted AO basis functions. There are two major steps in the calculation; evaluation of Eq. (8) to produce the final two electron integrals, and carrying out the transformations in Eq. (9) from the AO basis to MOs. The latter is performed sequentially, as in a conventional four index transform. The first step is:

$$A_{jl}(g) = \sum_k c_{kj} A_{kl}(g). \tag{10}$$

This step has a formal N^4 scaling which is reduced to N^3 by the use of integral cutoffs. However, this step has a very small prefactor, because the number of grid points N_g is much less than the square of the number of basis functions; additionally, vectorization and parallelization are straightforward because of the grid index. Consequently, this transform is not the rate limiting step in the calculation, as is demonstrated below.

The second step is:

$$A_{jq}(g) = \sum_l c_{lq} A_{jl}(g). \tag{11}$$

Note that at this stage one cannot introduce truncation of the virtual space because all pairs A_{jq} are needed for later calculations, due to the "exchange" terms in the local MP2 as discussed in detail below. The computational effort is then similar to step 1.

The final assembly of the two electron integrals, Eq. (8), has a formal scaling of $n^2 * N_v^2 * N_g$. As n and N_g are proportional to the size of the molecule, the approximate scaling with the number of atoms will be $\sim N_{atom}^3$. Increases in the basis set (fixing the molecule size) will primarily affect N_v, leading to an effective scaling of N^2 under these conditions. These scaling laws are obviously qualitative improvements over the N^3 or N_{atom}^5 obtained with conventional MP2 algorithms. Thus, if good accuracy can be obtained for reasonable grid sizes, the PS-LMP2 algorithm can be expected to qualitatively outperform existing MP2 codes. In the results section, we demonstrate that this is the case, obtaining large reductions in CPU time even in the ~ 20 atom range.

It is important to stress that the computational advantage of the pseudospectral LMP2 method over canonical MP2 and the analytic version of local MP2 lies in the the combination of the pseudospectral assembly of integrals and the local approximation. Regarding the comparison with analytic local MP2, the analytic formation of the K_{ij}^{pq} integrals for local MP2 requires a four index transformation discussed in Eqs. (6) and (7). Although this four index transormation to the local virtual space is faster than the full canonical four index transform it still retains nN^4 scaling in contrast to the N^3 pseudospectral scaling. The key to the pseudopectral efficiency is the ability to directly form the pseudopsectral integrals by multiplication in the local virtual space as in Eq. (8) rather than use sequential transformations in the AO space.

In addition to computational efficiency, it is important to consider disk storage and I/O requirements in evaluating a MP2 algorithm. In order for local MP2 to be tractable, the $n^2 N_v^2/2$ integrals over localized MOs must be able to fit on disk, otherwise it would be impossible to carry out the itera-

tive solve for the second order coefficients [Eq. (4)]. Fortunately the required disk storage scales as N_{atom}^2 and has a small prefactor. For example, a calculation involving a DZP basis and 200 occupied orbitals (i.e. 400 valence electrons, a very large system) would require only 500 MB of disk storage, an easily available amount when 1GB of disk for a workstation can be purchased for a few thousand dollars. For a massively parallel machine such as the IBM SP1, where each node has a large local disk, the integrals can be distributed over the nodes and hence very large systems can be studied.

The direct implementation of Eqs. (8) and (9) for canonical MP2 has been carried out by Martinez and Carter.[18] They obtained deviations up to 1.3 kcal/mol as compared with GAUSSIAN 92. These errors can be corrected by the use of the analytical corrections and length scales algorithms, modified to work efficiently in the MP2 computation. We give a brief description here of how this is accomplished.

2. Analytical corrections

The basic idea of the analytical correction scheme[19] is to calculate selected terms analytically and replace the pseudospectral terms with analytical ones. For LMP2, we calculate only one center and two center terms analytically. Furthermore, two center corrections for a given atom pair are made only when a localized molecular orbital has large amplitude on one of the atoms and the second atom is bonded to the first. This greatly reduces the number of two center corrections that are required (one center corrections are computationally trivial).

To efficiently implement analytical corrections, we form the correction matrices in the AO space of the virtual orbitals for each occupied pair (as opposed to the direct calculation in MO space described above) and carry out a conventional four index transform to produce the corrections in MO space. Thus, the initial quantity that is formed is:

$$K_{il}^{mn} = \sum_k c_{ki} K_{kl}^{mn}. \tag{12}$$

This is inexpensive because the set of AOs in Eq. (12) is highly restricted, as described above; the number of correction integrals required scales as N^2. Similarly, the four index transform exploits the restrictions on the AO indices for the initial steps and the restrictions on the virtual MO indices at later steps; the scaling of the transform is N^3. As demonstrated below, the prefactor associated with the corrections is also small; they consume only $\sim 10\%$ of the total CPU time for a medium sized (~ 30 atom) molecule, and this fraction diminishes as the molecule increases in size.

An important point is that the memory and disk storage required for the correction algorithm is minimal, as one stores only the nonzero correction matrices using a pointer structure for the data.

The Fock matrix is calculated pseudospectrally with limited analytic corrections as explained in Ref. 19. One-electron overlap, kinetic energy, and nuclear attraction integrals are evaluated totally analytically.

TABLE I. Pseudospectral canonical MP2 energies (a.u.) with (PSMP2) and without (PSMP2-nc) analytic correction integrals compared to all analytic MP2.

Molecule	MP2	PSMP2	Error(kcal/mol)	PSMP2-nc	Error(kcal/mol)
Water	−76.219740	−76.219713	0.02	−76.219822	0.05
Glycine	−283.643236	−283.643385	0.09	−283.643492	0.16
Dimet. Glyoxal	−305.585104	−305.585171	0.04	−305.581330	2.36
Methy Acetate	−267.617453	−267.617639	0.11	−267.617235	0.14
Ethanol	−154.568949	−154.568900	0.03	−154.569624	0.42

A measure of the importance of these analytic corrections can be obtained from Table I where pseudospectal canonical MP2 energies obtained with and without analytic corrections are compared to the all analytic Gaussian 92 MP2 energies with a 6-31G** basis. These and other results we have obtained with analytic corrections are typically within 0.2 kcal/mol of the all analytic energies while the pseudospectral errors without corrections can be as large as 1-2 kcal/mol. Note that the non-corrected reusults in Table I are not comparable to those of Martinez and Carter[18] since they did not use a length scales algorithm. Secondly we did not attempt to use the geometries of Ref. 18 and Ref. 18 correlated the 1s core while we did not.

3. Length scales algorithm

As explained in Ref. 17, one wishes to use a least squares fitting operator Q_i, where i is a diffuse AO, only when the three indices in front of Q are also diffuse. This is easily accomplished for LMP2 by dividing the transformed three center one electron integrals A_{jq} into a short (SR) and long range (LR) piece:

$$A_{jq}^{(SR)}(g) = \sum_{n=SR} c_{nq} A_{jn}(g);$$

$$A_{jq}^{(LR)}(g) = \sum_{n=LR} c_{nq} A_{jn}(g), \qquad (13)$$

$$A_{jq}^{(S+L)}(g) = A_{jq}^{(SR)}(g) + A_{jq}^{(LR)}(g),$$

where j,q are orbital indices and n is an AO index. Short range and long range classifications are assigned by the length scale of the AO basis functions. This requires no additional CPU time as each piece is simply accumulated separately.

The similar construction of long range and short range pieces for Q and R is similarly trivial. We then assemble the two electron integral over MOs as:

$$
\begin{aligned}
K_{ij}^{pq} = \sum_g & \{ [Q_p^{(SR)}(g) R_i^{(S+L)}(g) + Q_i^{(SR)}(g) R_p^{(LR)}(g)] \\
& \times A_{jq}^{(S+L)}(g) + [Q_j^{(SR)}(g) R_q^{(S+L)}(g) + Q_q^{(SR)}(g) \\
& \times R_j^{(LR)}(g) + Q_q^{(LR)}(g) R_j^{(LR)}(g)] A_{ip}^{(LR)}(g) \}.
\end{aligned}
$$

$$(14)$$

Roughly a factor of 2 in additional CPU time for the final assembly step is required by this modification of Eq. (8). It is possible that this can be dispensed with for weakly interacting pairs, a strategy we will investigate in the future. For the present, however, use of the length scales algorithm yields significant improvement in accuracy as has been demonstrated[17] in the Hartree–Fock case.

IV. RESULTS

A. Computational details

The local MP2 calculations were performed with the cc-pVTZ basis of Ref. 14 consisting of a $3s/2p$ contracted set on the H atom, a $4s/3p/2d$ set on C,N,O,F atoms and a $5s/4p/2d$ set on Cl. Note that we do not include f functions on any atom. For reference, the TZP basis used in Ref. 15 to which we compare our results has the same number of contracted functions as the cc-pVTZ basis but has a different primitive set and contraction scheme. The local MP2 calculations used the so called "ultra-fine" grid of the PSGVB (Ref. 20) code containing on average 400 grid points per atom. In addition limited one and two center corrections to the integrals were used as explained above. All MP2 calculations used a frozen 1s core for C,N,O,F atoms and a 10 electron frozen core for Si and Cl.

B. Water dimer

To test the PS-LMP2 code we have performed the LMP2 calculations on the water dimer reported in Ref. 12. Using the 6-311G(2d+p) basis and geometries of Ref. 12 we have calculated the LMP2 water dimer energy and have also calculated the counterpoise correction to the Hartree–Fock dimer energy. The results shown in Table II agree with those of Ref. 12 to within 0.2 kcal/mol. The small differences with the results of Ref. 12 result from the pseudospectral integration method. Further comparisons of our LMP2 code against the results of Pulay and Saebo are not possible since our

TABLE II. Pseudospectral water dimer energies (a.u.) and binding energies (kcal/mol) with HF counterpoise corrections compared to analytic (AN) results of Ref. 12.

Method	Monomer	Dimer	CP-corrected BE
HF PS	−76.043655	−152.095066	3.82
HF AN	−76.043687	−152.094995	3.78
PS LMP2	−76.257625	−152.524350	4.66
AN LMP2	...	−152.524620	4.84

TABLE III. Relative energies (kcal/mol) of small distortions of ethylene, acetic acid, and benzene calculated with local MP2 (LMP2) and canonical MP2.

Molecule	LMP2	MP2	Distortion
Ethylene	0.42	0.46	C-H symmetric stretch
	3.32	3.40	C-C stretch
	0.29	0.33	CH$_2$ stretch
Acetic Acid	51.37	51.00	CH$_3$ stretch
	0.45	0.54	O-H stretch
	3.09	3.08	C-O stretch
Benzene	38.6	39.5	local C-C distortion
	8.18	8.81	local C-C distortion
	57.75	58.35	local C-C distortion
	49.6	48.98	local C-C distortion
	2.38	2.39	C-H symmetric stretch
	0.33	0.26	C-H symmetric stretch

method currently correlates all valence pairs while Pulay and Saebo generally do not correlate all valence pairs.

C. Small displacements of atoms

To test the accuracy of the LMP2 method, we first have run a series of tests in which atoms are displaced by a small amount relative to a reference configuration. For these tests, we expect that the energy differences for canonical MP2 and LMP2 are extremely close. The results shown in Table III were obtained with a 6-31G** basis. The small distortions included symmetric stretches of H atoms and local distortions of a chosen atom. The results for ethylene, acetic acid and benzene show that LMP2 tracks canonical MP2 over a wide energy range of distortions. The results for benzene are particularly significant as it is commonly believed that benzene can only be described with delocalized symmetry orbitals. There is in fact no difficulty in converging the Boys localized orbitals of benzene and of course this unitary Boys localization does not change the physical observables of the HF wavefunction. The first order LMP2 wave function does however not retain the full D$_{6H}$ symmetry of the benzene ring. This point would perhaps be noticable in the LMP2 calculation of higher multipole moments though appears to be of no consequence for energy differences.

D. Conformational energies

The problem of calculating conformational energy differences is an extremely important one from the standpoint of molecular modeling. Such calculations are used routinely in the development of force fields, and errors in the quantum mechanical results represent a fundamental limitation on the accuracy of the molecular mechanics. While other errors in the force field are also of significance—for example, solvation effects, and nonbonded interactions—it is likely that errors in conformational energies are similar in magnitude.

In Ref. 15, the authors have assessed the performance of three computational models: canonical MP2, Hartree–Fock, and gradient-corrected density functional theory with TZP basis sets. In general the answers are quite reasonable; how-

ever, each method has a significant number of cases in which there is substantial disagreement with experiment. Hence, the problem cannot be said to have been solved in a completely reliable fashion.

In altering conformation, no chemical bonds are broken or formed. Consequently, one might expect that a perturbative method such as MP2 would yield rather accurate results. Indeed, a quite striking result of Ref. 15 (although not commented on by the authors) is that the difference between MP2 and MP4 results are in the vast majority of cases a few tenths of kcal/mol. This suggests that the problem cases in Ref. 15 may be a result of either inadequacies in the basis set or errors in the experimental numbers.

A major objective of the present section, in addition to validating the results from our LMP2 code, is to explore this possibility. Somewhat arbitrarily, we set 0.4 kcal/mol as our target for agreement of theory and experiment. A tighter range, which will certainly be warranted in the future, would require greater quality control with regard to the experimental data. In addition to presenting average theory/experiment deviations for various computational models, we examine cases where each of the methods deviate from experiment by more than this value, and attempt a preliminary judgement as to whether the problem is likely to arise from theory or experiment. The hope is that this rather provocative evaluation will spur experimentalists and theorists to focus on these cases and resolve the discrepancy one way or another, for example by newer, more accurate experiments (much of the data dates from 15–30 years ago) or by carrying out higher level correlated calculations with larger basis sets.

1. Conformational energy results

Table IV presents theory/experiment comparisons for the set of 36 molecules with experimental data considered in Ref. 15. In the non-cyclic molecules the conformers are typically of the gauche and anti form, while for the cyclic cases the substituent attached to the ring is in the equatorial or axial form. Further specification of the conformers can be obtained from Ref. 15.

In one set of runs (PSHF, LMP2 in Table IV) 6-31G* MP2 optimized geometries were used while in another set (PSHF-h, LMP2-h in Table IV) 6-31G* HF optimized geometries were used. For easy reference, we have included the canonical HF, MP2 and NLDA results of Ref. [15] (columns HF MP2 NLSDA in Table IV) where the MP2 was run at the 6-31G* MP2 optimized geometries, HF at the 6-31G* HF optimized geometries and the NLDA run at NLDA optimized geometries. In a few cases, we have recalculated canonical MP2 results with the Dunning cc-pVTZ basis (we did not do this for the entire set of molecules because of the computational expense). These cc-pVTZ MP2 results appear as the cc-pVTZ rows in Table IV. All experimental numbers are those listed in Ref. 15.

Our first goal is to identify cases where the experimental result is to be questioned, based upon all correlated theoretical methods (canonical MP2, LMP2, NLDA) yielding results that are very close to each other but quite different from the experimental values. As we have MP2 results here with two different basis sets and the NLDA results which calculate the

TABLE IV. Relative conformational energies (kcal/mol) from pseudospectral HF (PSHF) and local MP2 (LMP2) compared to HF, canonical MP2 and non-local spin density functional (NLSDA) calculations of Ref. 15. The cc-pVTZ rows refer to GAUSSIAN 92 HF and canonical MP2 with the cc-pVTZ basis.

Molecule	PSHF	PSHF-h	HF	LMP2	LMP2-h	MP2	NLSDA	Expt.
2-butene	1.74	1.75	1.54	0.90	1.39	1.31	0.93	1.0
ethanol	−0.18	0.20	0.30	0.10	0.11	−0.02	−0.34	0.12
cc-pVTZ			−0.17			0.05		
formic acid	5.01	5.07	5.70	4.30	4.62	4.94	4.61	3.90
glyoxylic acid	0.40	0.48	0.08	1.05	1.01	0.54	1.42	1.20
cc-pVTZ			0.42			1.30		
butane	1.09	1.06	0.96	0.66	0.92	0.61	0.67	0.75
N-methylacetamide	2.49	2.44	2.62	1.90	1.90	2.00	2.22	2.30
propylamine	0.54	0.4	0.61	0.18	0.19	0.28	0.39	0.42
isopropanol	0.31	0.32	0.38	0.30	0.26	0.23	−0.07	0.28
isoproplylamine	0.31	0.36	0.47	0.29	0.38	0.54	0.34	0.45
butanone	1.18	1.24	1.20	0.90	0.98	0.85	1.78	1.15,2.0
methyl vinyl ether	1.54	1.66	1.75	2.62	2.49	2.68	2.47	1.15
acrolein	2.39	2.39	2.07	2.20	1.83	2.12	2.23	2.0
propionaldehyde	0.81	0.82	0.74	0.75	0.76	0.84	0.82	0.95
1,3-butadiene	3.64	3.49	3.10	2.75	3.15	2.47	3.80	2.49
cc-pVTZ			3.44			2.80		
ethylether	1.75	1.67	1.76	1.00	1.29	1.49	1.13	1.10
isoprene	2.80	2.72	2.43	2.68	2.61	2.33	3.34	2.65
cyclohexamine	1.31	1.13	1.15	0.80	0.80	0.56	1.46	1.10
piperidine	0.78	0.88	0.95	0.60	0.66	0.87	0.64	0.4
cc-pVTZ			0.77			0.88		
methoxycyclohexane	0.89	0.61	0.57	0.30	0.27	−0.21	0.36	0.45
methoxytet.hydropan	0.46	0.74	1.06	1.22	1.19	1.49	1.11	1.05
N-methylformamide	1.00	1.66	1.01	1.13	1.20	1.21	1.58	1.45
1-butene	0.74	0.73	0.74	0.60	0.69	0.37	0.12	0.53
methyl formate	5.47	5.54	6.13	5.30	5.31	5.74	4.77	3.85,4.75
methyl ethyl ether	1.69	1.64	1.75	1.22	1.26	1.45	1.23	1.50
methyl acetate	8.80	8.85	9.42	7.65	7.74	7.80	7.20	7.5-8.5
cc-pVTZ			8.81			7.81		
2,3-dimethylbutane	−0.07	0.13	−0.11	−0.11	0.03	0.08	0.36	0.17
cyclohexanol	−0.27	−0.29	−0.34	−0.10	−0.15	−0.21	0.06	0.52
1,2-difluoroethane	0.07	0.14	−0.20	0.58	0.55	0.68	1.14	0.80
cc-pVTZ			0.17			0.61		
ethyl formate	0.69	0.61	0.67	0.29	0.25	0.22	0.38	0.19
fluoropropane	−0.02	0.14	0.04	0.39	0.08	0.05	0.05	0.35
methylcyclohexane	2.53	2.44	2.34	1.80	1.86	1.64	2.43	1.75
cyclohexane	6.99	6.87	6.75	6.23	6.24	6.22	6.15	5.50
N-methyl piperidine	3.97	3.93	3.93	3.46	3.41	3.65	3.15	3.15
1,2-dichloroethane	2.02	1.92	1.92	1.31	1.54	1.29	1.49	1.20
cc-pVTZ			1.98			1.41		
chloropropane	0.43	0.35	0.37	−0.16	−0.27	−0.13	0.29	−0.05
cc-pVTZ			0.35			−0.13		
dimethyl dioxane	1.30	1.09	1.07	0.85	0.74	0.47	1.16	0.90

[a]PSHF, MP2, and LMP2 use 6-31G* MP2 optimized geometries while HF, HF-h and LMP2-h values used the 6-31G* HF optimized geometries. NLSDA uses NLSDA optimized geometries.

correlation energy in a very different manner, it would be remarkable for all of the theoretical calculations to accidentally yield the same incorrect value. Three molecules immediately can be seen to fall into this category: methyl vinyl ether, cyclohexane, and cyclohexanol. In all cases, the theoretical calculations are within a few tenths of a kcal/mol whereas the experimental data differs from all of the theoretical results by more than 0.5 kcal/mol (for methyl vinyl ether, the devation is ∼1.5 kcal/mol). In the case of cyclohexanol, the ''experimental'' reference in Ref. 15 was in fact a theory paper which itself referenced an experimental paper: we were unable to find the quoted value, 0.52 kcal/mol, anywhere in this paper. For the other two cases the experiments were carried out more than 15 years ago and their accuracy is

unclear, as modeling is required to interpret the experimental data. We believe that these cases are deserving of experimental reexamination (although higher levels of theory should also be tried—it is noteworthy that the energy difference for methyl vinyl ether diminished by 0.4 kcal/mol, a rather large result, using MP4 corrections).

We next consider cases where there are large experimental error bars, for one reason or another, and one cannot choose between the values based upon agreement of the theoretical methods. The first case is methyl acetate: due to the large magnitude of the energy difference, the population of the high energy conformer was quite small, and the authors estimate their uncertainty as +/− 1 kcal/mol. We note that there is a large basis set dependence of the MP2 results

TABLE V. Average and rms deviations of the conformational energy differences (kcal/mol) of the previous table from experiment.

Error	PSHF	PSHF-h	HF	LMP2	LMP2-h	MP2	NLSDA
Full Ave.	0.49	0.41	0.48	0.27	0.31	0.36	0.36
Full RMS	0.59	0.54	0.65	0.39	0.42	0.49	0.50
Filtered[a] Ave.	0.48	0.39	0.31	0.18	0.23	0.31	0.28
Filtered[a] RMS	0.56	0.50	0.62	0.22	0.29	0.41	0.39

[a]The filtered average removes six cases (see text) for which the experimental values are questioned.

here, with a change of 0.5 kcal/mol going from the TZP basis of Ref. 15 to the cc-pVTZ basis. The second case is cyclo-hexamine. Both LMP2 and the NLDA are more or less within the range of values given here, 1.1–1.8 kcal/mol, by our criterion. The third, and perhaps most interesting case, is butanone. Here there are two experimental values, one of which agrees with MP2 results and the other of which agrees with NLDA results.

In computing average errors, one has to make some sort of decision about what the "experimental" value is. Below, in our unfiltered average error statistic (no molecules discarded) we assign the most favorable error possible for each method for the three above cases. In our filtered average error statistic, we remove these three cases as well as the three cases where we question the experiments from the data set, leaving 30 molecules in all.

Table V presents inclusive and filtered average errors and standard deviations for each of the methods presented in Table IV (excluding the cc-TZVP canonical MP2 calculations, for which we do not have a full data set). The LMP2 results are superior even for the unfiltered case, and become qualitatively superior for the filtered set. Indeed there is only one molecule, methyl formate, for which the LMP2 results deviate from experiment by more than 0.4 kcal/mol (the deviation is 0.55 kcal/mol), while the NLDA displays errors this large in six cases (formic acid, 1,3-butadiene, isoprene, ethanol, 1-butene and methylcyclohexane).

The results for molecules which are qualitatively in error in the MP2 calculations of Ref. 15, such as glyoxylic acid, methoxycyclohexane, and dimethyl dioxane, display excellent agreement in our LMP2 calculations. For glyoxylic acid the canonical MP2 error is greatly reduced from 0.6 kcal/mol to 0.1 kcal/mol by using the cc-pVTZ basis. The other two molecules methoxycyclohexane and dimethyl dioxane were not run with the cc-pVTZ basis due to the large computational expense of GAUSSIAN 92 with this basis, however, it is plausible that the MP2 results for these molecules could be similarly improved with cc-pVTZ basis. The other possibility is that the MP2 errors in methylcyclohexane and dimethyl dioxane are a result of BSSE. The resolution of the MP2 error here requires further study, however, given the relatively good agreement between LMP2 and MP2 for the other molecules we are inclined to believe that the cc-pVTZ basis could account for the difference between MP2 and LMP2 for these two molecules.

The LMP2 results using the 6-31G* HF optimized geometries differ in most cases from the 6-31G* MP2 optimized geometries by of order 0.1 kcal/mol with a maximum

TABLE VI. CPU times (minutes) for pseudospectral HF and LMP2 compared to GAUSSIAN 92 HF and MP2. N_{bas} is the number of basis functions and N_{occ} the number of occupied orbitals correlated.

Molecule	N_{bas}	N_{occ}	T-G92HF	T-PSHF	T-G92MP2	T-LMP2
			cc-pVTZ basis IBM-370[a]			
1,3-butadiene	146	11	25	10	50	15
methyl acetate	169	15	51	18	134	23
butanone	197	15	72	35	210	30
piperidine	237	18	170	43	1037	55
			6-31G** basis IBM-580[b]			
Alinine	160	23	13	5	34	17
Leucine	200	27	26	10	90	30
Arginine	250	35	37	17	234	50
Si_4Me_{10}	392	43	120	30	1740	154
Porphine	430	56	167	60	1800	270

[a]G92-MP2 and PS-LMP2 scaling exponents for this set are 4.9 and 2.6, respectively.

[b]G92-MP2 and PS-LMP2 scaling exponents for this set are 4.0 and 2.8, respectively.

deviation of 0.5 kcal/mol. However, for 2-butene, 1,3-butadiene, and fluoropropane the 6-31G* MP2 optimized geometries do yield noticable improvements over the results obtained from the HF geometries. These results suggest that MP2 geometry optimization while not essential to obtaining accurate results in most cases, can reduce any substantial errors caused by the HF geometries. We intend to study the importance of geometry optimization further when the local MP2 gradient program we are developing is completed.

The conclusion of our calculations is thus quite different from that of Ref. 15. There, it was argued that the NLDA results were comparable in accuracy to MP2. Here, it is clear that MP2, when used with a sufficiently good basis set, is significantly more reliable (and may, in fact, prove to be qualitatively superior, providing accurate answers in all cases, when the reliability of the experimental data are sorted out). However, this should not detract from the impressive performance of the NLDA methods, which are a very large improvement over the LDA approach. Also, one clearly ought to check the basis set dependence of the NLDA calculations as this may eliminate some errors as it has done for MP2.

V. TIMING COMPARISONS

Timings for pseudospectral HF and local MP2 are displayed in Table (VI) in comparison to GAUSSIAN 92 HF and MP2. Tests were run for up to 430 basis functions and 56 correlated orbitals on IBM workstations. The first timing comparison used the cc-pVTZ basis and an IBM-370 with 64 MB of memory while the second comparison used a 6-31G** basis and an IBM-580 with 256 MB memory. Since canonical MP2 uses an inordinate (n^2N^2 words for n occupied orbitals) amount of disk space for these systems, GAUSSIAN 92 was run in "direct" mode and tests on arginine indicated that GAUSSIAN 92 MP2 in disk or semi-direct mode is no faster than in direct mode. Both PSGVB and GAUSSIAN 92 were run in C1 symmetry. A test of GAUSSIAN 92 with C2 symmetry for Si_4Me_{10} only lowered the cpu time by 10%, most likely a result of the four-index transformation domi-

TABLE VII. CPU times (IBM-370 minutes) for LMP2 construction of integrals (T-INT) and the time spent in the iterative solution (T-SOLV) of the first-order coefficients for the cc-pVTZ cases of the previous table.

Molecule	N_{bas}	N_{occ}	T-INT	T-SOLV
1,3-butadiene	146	11	12.3	2.0
methyl acetate	169	15	19.0	3.1
butanone	197	15	24.0	4.1
piperidine	237	18	47.2	5.8

nating the MP2 cpu time where symmetry is not used. We note that attempts to run larger GAUSSIAN 92 cc-pVTZ cases on the IBM-370 generally ran into memory problems and attempts to run porphine and Si_4Me_{10} with GAUSSIAN 92 on an IBM-370 indicated of the order of a factor of 10 increase in CPU time for the MP2. In contrast the PS-LMP2 CPU time varies by no more than a factor of 1.5 between a 256-MB IBM-580 and a 64-MB IBM-370.

The local MP2 has extremely good scalings of 2.8 and 2.6 compared to GAUSSIAN 92 MP2 scalings of 4.0 and 4.9 in the 6-31G** and cc-pVTZ basis respectively. The local MP2 scaling is in the range of the 2.9 NLDA scaling of Ref. 15.

Table VII provides a representation of the relative time spent in constructing the K_{ij}^{pq} integrals of Eq. (14) and the time spent in the iterative solution of Eq. (4). The iterative solve which typically takes five iterations to converge the energy to 1×10^{-5} a.u. consumes from 10% to 15% of the LMP2 time. For a fixed basis type correlating n orbitals the LMP2 solver exhibits an $n^{2.8}$ scaling while for fixed n and variable basis type or variable virtual space size N_v, the solver scales as $N_v^{2.5}$. The K_{ij}^{pq} construction scales as $N^{2.75}$.

Finally we compare local MP2 timings with GAUSSIAN 92/DFT DFT times in Table VIII on an IBM-530 with the cc-pVTZ basis. The LMP2 itself is faster than GAUSSIAN 92/DFT DFT with, as noted above, both methods having similar scalings. Adding the Hartree-Fock time to the LMP2 time makes the total LMP2 calculation time equal to the DFT time for the first three cases while for piperidine HF+LMP2 is 25% faster than DFT. This preliminary test indicates that LMP2 is no more costly than DFT.

The timing results presented here should be regarded as provisional. Optimization of parameters specifically for MP2 (e.g. grid and dealiasing parameters) and the use of a multi-grid algorithm will result in significant gains. More importantly, it should be possible to carry out computations on weakly coupled pairs, which do not contribute significantly to the energy, inexpensively using smaller grids and fewer

TABLE VIII. CPU times (minutes) for pseudospectral HF and LMP2 (HF + LMP2 totals denoted by T-(HF+LMP2)) compared to GAUSSIAN 92 DFT using the cc-pVTZ basis set on an IBM-530.

Molecule	cc-pVTZ basis IBM-530				
	N_{bas}	N_{occ}	T-PSHF	T-LMP2	T-(HF+LMP2)	T-DFT
1,3-butadiene	146	11	14	20	34	30
methyl acetate	169	15	20	30	50	55
butanone	197	15	28	39	67	76
piperidine	237	18	46	90	136	173

analytic corrections in the calculation of the integrals coupling these pairs. We estimate that an implementation of this strategy could reduce the CPU times reported here by as much as a factor of 2. However, the greatest impact will be in the scaling with system size which, for large systems, should behave asymptotically as $\sim N^2$.

VI. CONCLUSION

In this paper, we have demonstrated that the PS-LMP2 methodology is an efficient and highly accurate approach to the calculation of gas phase conformational energies of organic molecules. The order of magnitude performance enhancement as compared to canonical MP2, without loss of accuracy (if anything, greater accuracy is attained) suggest that the latter method has essentially been rendered noncompetitive. There may be other efficient approaches to coding LMP2, based upon the conventional two electron integral generation schemes: however, this has not yet been demonstrated.

The comparison of gradient corrected DFT and LMP2 is less clear. While the results presented here favor LMP2 with regard to accuracy, and the CPU times for both method are comparable, there is a lot of room for improvement of the DFT approach with regard to both accuracy and efficiency. Firstly, we have not tested all of the available DFT approaches; for example, the mixed HF/DFT method of Becke[21] may prove to be better suited to conformational energy calculations than the gradient corrected NLDA approach examined here. Secondly, new functionals are continually being developed and refined; as these are targeted towards the type of problems examined here, they are likely to become increasingly accurate. Finally, substantial improvements in the numerical algorithms for solving the DFT equations are quite feasible; we are currently in the process of adapting PS methods to DFT calculations.

The present set of test cases, while sufficient to draw the conclusions described above, are by no means comprehensive. Tests on larger molecules need to be carried out. Molecules incorporating atoms across the entire periodic table must be examined. Our study of dispersion interactions and hydrogen bonding here is quite cursory; extensive sets of test molecules need to be assembled which cover these areas thoroughly. Nevertheless, the present results are encouraging, and suggest that MP2 with large basis sets will be a computationally practical and chemically predictive tool for wide classes of problems.

In the very near future, we will have available methods in which LMP2 is carried out from a multiconfigurational, rather than Hartree-Fock, reference. These GVB-RCI-MP2 methods have already been shown[8,9] to yield high accuracy even for bond-breaking processes. Furthermore, we have shown[3] in a previous publication that computational scaling $\sim N^3$ of the MCSCF part of the calculation can be attained, and that overall CPU times on workstations for large molecules are reasonable. Thus, this methodology will be applicable to large molecules.

With regard to the results presented here, we will be able to test some of the cases in which we have suggested that the experiments are problematic, or where there is a disagree-

ment between DFT and LMP2 calculations and the experiments are ambiguous. If the results remain constant when the level of correlation is increased to the RCI-MP2 level, and use of larger basis sets also fails to change the results, the validity of the LMP2 values will be confirmed; on the other hand, it may well be that for some of these cases there are substantial higher order effects that will be obtained in an RCI-MP2 calculation.

ACKNOWLEDGMENTS

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