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Møller–Plesset correlation energies in a localized orbital basis using a Laplace transform technique

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Summary. In electronic structure calculations requiring the handling of large amounts of integrals, storage requirements can often be reduced through the use of localized orbitals which gives rise to sparse integral arrays. However, conventional Møller–Plesset perturbation theory is constrained to canonical orbitals due to the explicit use of orbital energies in the energy expressions, and it is therefore not straightforward to reduce the storage requirements through such orbital localization. This work shows how the constraint of canonical orbitals can be lifted using a Laplace transform technique, and investigates the reduction in storage requirement that can result from the localization of orbitals made possible by such an approach.

Key words: Laplace transform – MP2 – *ab initio* correlated method – Localization – Electronic structure calculations

1 Introduction

Recent developments of direct methods [1–3] for electronic structure calculations have allowed the application of rigorous *ab initio* theory to molecules of a size which was unthinkable only a few years ago [4]. Direct methods have now been implemented both in Hartree–Fock and in several correlated schemes [1–3, 5]. However, even with direct methods, the steep scaling of correlation methods remains a bottleneck for routine calculations of large molecules. This problem is even encountered at the simplest correlated level, second-order Møller–Plesset perturbation theory (MP2), which scales as N^5. In this method, the transformation time for medium-sized systems is often overshadowed by the integral evaluation time, which has a lower power dependence but a much larger prefactor. For large systems the time is dominated by the transformation, due to its nominal N^5 dependence and the absence of any significant benefit from integral prescreening in that part of the calculation.

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To extend calculations such as these to large systems, methods which result in sparse arrays of transformed integrals are of great interest, as this would allow significant compression of the integrals. Localization of the orbitals can accomplish such sparsity, resulting in savings in the storage requirement as well as in CPU time. However, the standard formulation of Møller–Plesset theory refers to canonical orbitals, and prevents any simple localization.

Fortunately, there are available methods which circumvent this canonical formulation, allowing localization of the orbitals to be utilized. One such approach used to reduce storage bottlenecks is the local correlation scheme developed by Saebo and Pulay [6]. As applied to MP2, a form of the MP2 expression is used which is invariant to rotations among the occupied and virtual orbitals. The occupied space is localized by conventional means, and the virtual space used to correlate each occupied pair is defined as the subspace of the atomic orbitals that are spatially close to the localized occupied orbitals. While this method has undisputed promise for treating large systems, it is difficult to strictly monitor the accuracy of the approximation made in the truncation of the virtual space to a subset of the AO basis [7].

Here, we discuss a similar method which reduces the virtual space based on rigorous integral thresholds, allowing the approximation to be strictly monitored with regard to its effect on the final total energy. We use the Laplace formulation [8, 9] in order to provide an invariant form of the MP2 expression which is described in the following section. Additionally, we have investigated several localization schemes and screening criteria, and examined their effectiveness in the context of Laplace MP2 [10].

2 Laplace transform techniques

The second-order correction to the electronic energy can be expressed in a spin orbital formalism as

$$E^{(2)} = -\frac{1}{4}\sum_{ijab} \frac{\langle ab \| ij\rangle^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \tag{1}$$

where

$$\langle ab \| ij\rangle = \langle ab | ij\rangle - \langle ab | ji\rangle, \tag{2}$$

$$\langle ab | ij\rangle = \int \psi_a^*(1)\psi_b^*(2)\frac{1}{r_{12}}\psi_i(1)\psi_j(2)\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2; \tag{3}$$

$i, j, \ldots$ denote occupied molecular orbitals, and $a, b, \ldots$ denote virtual orbitals. In order to lift the constraint of canonical orbitals, the energy denominators in Eq. (1) can be rewritten using a Laplace transform [8, 9]

$$(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)^{-1} = \int_0^\infty \mathrm{e}^{-(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t}\,\mathrm{d}t \tag{4}$$

and the correlation energy can thus be expressed as

$$E^{(2)} = \int_0^\infty e^{(2)}(t)\,\mathrm{d}t, \tag{5}$$

where

$$e^{(2)}(t) = -\frac{1}{4}\sum_{ijab} \langle ab \parallel ij \rangle^2 \, \mathrm{e}^{-(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)t} . \tag{6}$$

So far, little has been gained compared to the original expression (1). However, with this new formulation of the correlation energy, $e^{(2)}$ can be written in terms of t-dependent orbitals and integrals. To accomplish this, a t-dependent scaling of the orbitals is introduced as follows:

$$\psi_i(t) = \psi_i(0)\, \mathrm{e}^{\varepsilon_i t/2} \tag{7}$$

for the occupied orbitals, and

$$\psi_a(t) = \psi_a(0)\, \mathrm{e}^{-\varepsilon_a t/2} \tag{8}$$

for the virtuals, $e^{(2)}$ can now be written as

$$e^{(2)}(t) = -\frac{1}{4}\sum_{ijab} \langle a(t)b(t) \parallel i(t)j(t) \rangle^2 . \tag{9}$$

Equation (9) is invariant under unitary rotations within both the occupied and the virtual orbital space of scaled orbitals [11], and this invariance can be exploited to localize the orbitals, leading to improved sparsity of the transformed integral arrays and reducing the number of integrals that must be stored.

3 Numerical quadrature

For the final evaluation of the correlation energy (5), a numerical quadrature scheme must be used. Fortunately, the function $e^{(2)}(t)$ in Eq. (9) is well behaved and monotonically decreasing, as illustrated in Fig. 1 for a calculation on *p*-chloro-phospha-benzene. In fact, for most systems $e^{(2)}$ is virtually indistinguishable from a simple exponential function, and one would therefore not expect the numerical integration to be a major computational obstacle.

In principle, any quadrature scheme could be used for the evaluation of Eq. (5), but in the interest of efficiency we seek one with the minimum number of

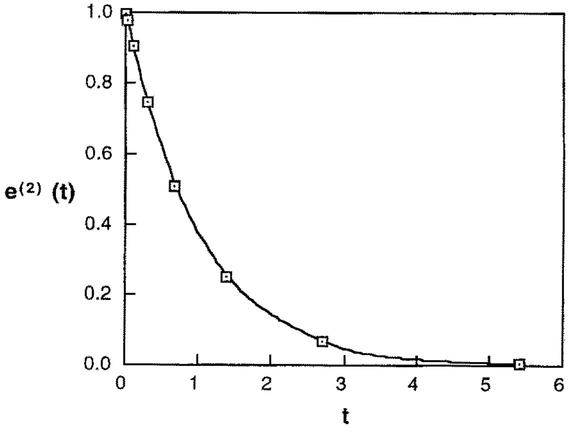

Fig. 1. An illustration of the decay of the function $e^{(2)}(t)$ with the value of t, demonstrating why an efficient quadrature scheme can be designed so easily. The figure shows $e^{(2)}(t)$ for *p*-chloro-phospha-benzene. The optimum quadrature points are also indicated

quadrature points (since a complete integral transformation must be carried out for each point). In a conventional numerical quadrature scheme the integral would be approximated with a quadrature in n points as

$$\frac{1}{x_{abij}} = \sum_{\alpha=1}^{n} w_\alpha \mathrm{e}^{-x_{abij} t_\alpha}, \tag{10}$$

where we have used $x_{abij} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$, and where the quadrature points t_α and weights w_α can be optimized in order to find the best fit for $1/x$. This is done using a least-squares approximation

$$\sum_{ijab} \left(\frac{1}{x_{abij}} - \sum_{\alpha=1}^{n} w_\alpha \mathrm{e}^{-x_{abij} t_\alpha} \right)^2 = \min!\,. \tag{11}$$

The procedure can thus also be viewed as an approximation of $1/x$ with a basis set expansion in exponential functions. Clearly, it is sufficient for the approximation to be accurate over an interval ranging from $X_{\min} = \min(x_{abij})$ to $X_{\max} = \max(x_{abij})$.

$$\int_{x_{\min}}^{x_{\max}} \left(\frac{1}{x} - \sum_{\alpha=1}^{n} w_\alpha \mathrm{e}^{-x t_\alpha} \right)^2 \mathrm{d}x = \min!\,. \tag{12}$$

The weights w_α can be determined for each of the exponential factors t_α by solving the equation

$$\boldsymbol{B}\boldsymbol{w} = \boldsymbol{a}, \tag{13}$$

where

$$a_\alpha = \int_{x_{\min}}^{x_{\max}} \frac{1}{x} \mathrm{e}^{-x t_\alpha} \, \mathrm{d}x, \tag{14}$$

$$B_{\alpha\beta} = \int_{x_{\min}}^{x_{\max}} \mathrm{e}^{-x(t_\alpha + t_\beta)} \, \mathrm{d}x\,. \tag{15}$$

The optimum exponents t_α can be determined with a similar, non-linear least-squares procedure. The final expression for the MP2 energy is thus

$$E^{(2)} \approx \sum_{\alpha=1}^{n} w_\alpha e^{(2)}(t_\alpha) = -\frac{1}{4} \sum_{ijab} \sum_{\alpha=1}^{n} w_\alpha \langle a(t_\alpha) b(t_\alpha) \parallel i(t_\alpha) j(t_\alpha) \rangle^2, \tag{16}$$

with $e^{(2)}$ evaluated as in Eq. (9). A detailed discussion of these methods is given in Ref. [9].

4 Laplace transforms in MP2 calculations

As test cases of the quadrature scheme, fluorobenzene and fluoronaphthalene were chosen. For an unbiased comparison, point group symmetry was not used in the integral evaluation or transformation. The calculations were performed in a DZP basis set [12] with the core orbitals uncorrelated.

The number of points required to achieve a certain accuracy in the correlation energy was determined by optimizing the fit in Eq. (11) using a Mathematica procedure [13]. In the evaluation of Eq. (5), $x_{\min}$ and $x_{\max}$ correspond to twice the HOMO-LUMO and LOMO-HUMO intervals, respectively. The resulting points and weights $\{t_\alpha, w_\alpha\}$ for fluorobenzene are given in Table 1, while Table 2 presents the corresponding data for fluoronaphthalene.

Table 1. The integral in Eq. (12) was evaluated for fluorobenzene in a DZP basis over the interval $\{x_{\min}, x_{\max}\} = \{0.9150, 113.7062\}$. The resulting exponential coefficients t_α and weights w_α are given in the table. n is the number of quadrature points used in the evaluation of $1/x$

n		$\alpha = 1$	$\alpha = 2$	$\alpha = 3$	$\alpha = 4$	$\alpha = 5$	$\alpha = 6$	$\alpha = 7$	$\alpha = 8$
1	t	0.258947							
	w	0.884074							
2	t	0.039060	0.588206						
	w	0.131312	1.348680						
3	t	0.018190	0.183415	1.097040					
	w	0.054369	0.357190	1.838180					
4	t	0.012422	0.094861	0.432693	1.694440				
	w	0.034548	0.156628	0.614631	2.261590				
5	t	0.009594	0.063251	0.236842	0.768159	2.347860			
	w	0.025822	0.092434	0.290636	0.872647	2.628780			
6	t	0.007868	0.047974	0.157484	0.443380	1.173410	3.041960		
	w	0.020834	0.064754	0.170794	0.442272	1.119560	2.953180		
7	t	0.006686	0.039006	0.117644	0.298135	0.709292	1.635110	3.766920	
	w	0.017543	0.050084	0.115876	0.265378	0.601198	1.351750	3.244240	
8	t	0.005820	0.033056	0.094392	0.221653	0.485187	1.028230	2.143140	4.516430
	w	0.015186	0.041110	0.086569	0.179157	0.370673	0.761242	1.568940	3.508800

Table 2. The integral in Eq. (12) was evaluated for fluoronaphthalene in a DZP basis over the interval $\{x_{\min}, x_{\max}\} = \{0.7189, 113.7109\}$. The resulting exponential coefficients t_α and weights w_α are given in the table. n is the number of quadrature points used in the evaluation of $1/x$

n		$\alpha = 1$	$\alpha = 2$	$\alpha = 3$	$\alpha = 4$	$\alpha = 5$	$\alpha = 6$	$\alpha = 7$	$\alpha = 8$	$\alpha = 9$
1	t	0.258947								
	w	0.884074								
2	t	0.037199	0.577046							
	w	0.126181	1.335430							
3	t	0.015572	0.167388	1.050350						
	w	0.047392	0.335889	1.799520						
4	t	0.010402	0.083007	0.397673	1.618360					
	w	0.029238	0.141347	0.582494	2.213200					
5	t	0.007960	0.053930	0.210387	0.709565	2.240140				
	w	0.021549	0.080823	0.266943	0.831566	2.572960				
6	t	0.006498	0.040315	0.136524	0.398143	1.088470	2.901730			
	w	0.017269	0.055437	0.152827	0.410847	1.071490	2.891650			
7	t	0.005507	0.032504	0.100299	0.261830	0.642029	1.521830	3.593430		
	w	0.014486	0.042299	0.101545	0.241105	0.562981	1.298080	3.178010		
8	t	0.004786	0.027405	0.079575	0.191408	0.430395	0.936459	2.000100	4.309070	
	w	0.012509	0.034416	0.074653	0.159730	0.340420	0.717187	1.510710	3.438560	
9	t	0.004235	0.023779	0.066308	0.150284	0.315595	0.640655	1.275540	2.515490	5.043720
	w	0.011028	0.029179	0.058847	0.115630	0.227859	0.446795	0.870323	1.710640	3.678790

The MP2 energies obtained using the quadrature (13) with the data from Tables 1 and 2 are reported in Table 3 for fluorobenzene and fluoronaphthalene. Additionally, the error as compared to the conventional contribution is provided. Clearly, milli-Hartree accuracy can be obtained with only four quadrature points. (The lack of perfectly monotonic convergence with increasing n is due to the fact that the fit (Eqs. (11) and (12)) does not take the integral values and the distributions of x_{abij} into account. Thus, while the fit of $1/x$ to the sum of exponentials always improves monotonically – in a least-squares integral sense – with increasing n, the approximation in Eq. (16) is not guaranteed to do so. Ultimately, as n grows beyond limits convergence is of course always guaranteed.)

In order to simplify the approach, we examined the possibility of using one unique set of quadrature points for a number of systems. We used the set of eight quadrature points developed in Ref. [9] for the medium-sized system *p*-chlorophospha-benzene in calculations on the six systems fluorobenzene, fluoronaphthalene, fluoroanthracene, fluoronaphthacene, fluoropentacene, and fluorohexacene. A STO-3G basis [14] was used for all these systems since it allowed access to extended systems at a low cost, and since agreement with experimental results was not an issue here. As shown in Table 4, using one set of quadrature points for various systems is definitely a viable approach. Even for the largest test system, fluorohexacene, milli-Hartree accuracy is achieved with eight quadrature points or less.

Table 3. MP2 energies and relative errors for a varying number of quadrature points n for fluorobenzene and fluoronaphthalene. A DZP basis was used

n	Fluorobenzene		Fluoronaphthalene	
	Correlation energy	Relative error	Correlation energy	Relative error
1	−1.060099	1.3×10^{-1}	−1.642201	1.3×10^{-1}
2	−0.931256	8.9×10^{-3}	−1.453216	2.1×10^{-3}
3	−0.934505	5.4×10^{-3}	−1.444828	7.9×10^{-3}
4	−0.939438	2.1×10^{-4}	−1.455377	6.4×10^{-4}
5	−0.939619	1.5×10^{-5}	−1.456032	1.8×10^{-4}
6	−0.939587	4.9×10^{-5}	−1.456105	1.4×10^{-4}
7	−0.939631	1.9×10^{-6}	−1.456239	4.3×10^{-5}
8	−0.939683	5.3×10^{-5}	−1.456269	2.3×10^{-3}
Exact	−0.939633	—	−1.456302	—

Table 4. Conventional MP2 correlation energy contributions (in mE_h) and the error (absolute) in a Laplace MP2 calculation using eight quadrature points

Molecular system	Conventional MP2	Error with Laplace MP2
Fluorobenzene	−347.246908	4.70×10^{-5}
Fluoronaphthalene	−590.121092	2.75×10^{-4}
Fluoroanthracene	−834.882267	1.22×10^{-2}
Fluoronaphthacene	−1076.198480	4.80×10^{-2}
Fluoropentacene	−1315.876443	1.12×10^{-1}
Fluorohexacene	−1556.003770	2.03×10^{-1}

Still, the best accuracy with the least number of points is expected if the points and weights are actually determined for the system under consideration. It must be determined on a case-by-case basis if an optimum quadrature for each system is worth the extra effort of determining specific quadrature points and weights for the orbital energy interval in question. Obviously, the success of the above simplified approach hinges on the fact that the $\{x_{\min}, x_{\max}\}$ interval of the system for which the quadrature points and weights were determined covers that of all the systems that were actually studied. If the system under consideration has x_{abij} values in a range for which no particular accuracy of the approximation (11) is guaranteed by the least-squares procedure, one cannot expect reliable results.

The numerical evaluation of the invariant MP2 expression requires an individual evaluation and integral transformation for each quadrature point. For instance, using an eight-point quadrature requires going through the transformation eight times. Simply using the Laplace formulation will therefore increase the number of integrals that must be evaluated and processed by that factor. However, the invariant property of the expression allows localization of orbitals which will reduce the number of large integrals that must be handled, hopefully, even beyond the number in canonical MP2.

5 Localization methods

To exploit the invariance of Eq. (9) for reducing storage and simplifying the calculations, the orbitals need to be localized. Any reasonable localization of the orbitals is likely to increase the sparsity of the integral arrays, and can thus be useful for reducing storage requirement (and perhaps also CPU-requirement). However, in order to maximize the sparsity of the integral arrays, localization methods that specifically provide the maximum number of negligible two-electron integrals $\langle ij|ab\rangle$ should be sought. For large systems the coulomb-type terms $\langle ij|ab\rangle\langle ij|ab\rangle$ in the MP2 energy expressions are typically more significant in terms of size than the exchange-type terms $\langle ij|ab\rangle\langle ij|ba\rangle$, and in the present work we focus on localization schemes which address the former.

For the localization of occupied orbitals, several standard schemes have been proposed in the literature [15–17] and the choice between these has little impact on the performance of the present approach. For efficiency reasons the Boys method [15], which localizes orbitals based on orbital centroids, and the Pipek–Mezey method [17] based on gross atomic populations, have been used in the present work.

For the localization of virtual orbitals, different approaches were also used. A simple Boys localization of the full virtual orbital space is referred to as a global approach. In addition, two "local" approaches have been investigated, both of which can be viewed as modifications of the Edmiston–Ruedenberg approach [16]. In the first, a separate localization of the entire virtual orbital space is performed for every unique pair of occupied orbitals, and in the second, the entire virtual space is localized for each particular occupied orbital. The coulomb-like part of the correlation energy

$$\sum_{ab} \langle ab|ij\rangle^2 \tag{17}$$

is invariant under unitary rotations of the virtual orbitals, and a large number of small terms in the sum thus necessitates a few large ones. Accordingly, a localization technique that provides either large or negligible $\langle ab|ij\rangle$ is of interest. A sum of the squares of these terms is not invariant, and maximizing such a sum would have the desired effect of creating either large or negligible terms in Eq. (17). In the present work we have used a method which maximizes the sum of squares of the coulomb-type term for each unique pair of occupied orbitals

$$R_{ij} = \sum_{ab} \langle ab \,|\, ij \rangle^4 . \tag{18}$$

The virtual orbitals which maximize R_{ij} are determined by using a standard Newton–Raphson procedure to optimize an exponentially parametrized unitary transformation [18]. This requires an iterative procedure. Since a full localization must be carried out for each occupied pair, a diagonal approximation to the Hessian is used in the Newton scheme for reasons of computational economy. The approximate nature of this approach does not affect the final result as long as the scheme converges, but it can affect the rate of convergence.

Orbitals are rotated one pair at a time (2 × 2 rotations) as in other localization schemes [16] rather than using the entire U matrix to accomplish the localization. R_{ij} is successively maximized for each chosen pair of orbitals. This iterative procedure converges to a maximum in the same way as a Jacobi diagonalization procedure.

In a simplified version of this scheme, the virtual space is localized with respect to a single occupied orbital. This also provides small differential overlaps between occupied and virtual orbitals, even though the $\langle ab \,|\, ij \rangle$ integrals are not addressed directly. In analogy with the previous method, the expression

$$\sum_{a} \langle aa \,|\, ii \rangle \tag{19}$$

is invariant under unitary transformations of the virtual orbitals, and a maximization of the sum of squares

$$R_i = \sum_{a} \langle aa \,|\, ii \rangle^2 \tag{20}$$

thus provides many small contributions to Eq. (19). Again, a Newton–Raphson approach has been used to maximize R_i. In this scheme, however, it is not cost prohibitive to use the full Hessian since fewer localization steps are needed and since the Hessian only has N^3 independent terms rather than N^4 as in the previous scheme. Further details of these methods are provided in Ref. [18].

6 Localization in a Laplace scheme

The convergence behavior of the virtual localization with respect to each occupied orbital pair is illustrated in Fig. 2 for the three smallest test systems. Shown is the number of large contributions ($> 10^{-8}$ E_h) at convergence cutoffs of 200, 1000, and 6000 2 × 2 rotations for each occupied orbital pair. The cutoffs are used to keep the calculation from becoming too expensive in terms of CPU time. The number of 2 × 2 rotations for this method, illustrated in Table 5, is comparable to the number required in the occupied orbital localization. A localization of the occupied orbitals for fluorobenzene requires over 30 cycles where each cycle includes 18 2 × 2 rotations. For large t_α values most of the orbitals are scaled down to insignificance and their localization encounters numerical challenges which has lead to the increased number of 2 × 2 rotations seen in Table 5. According to Fig. 2, the

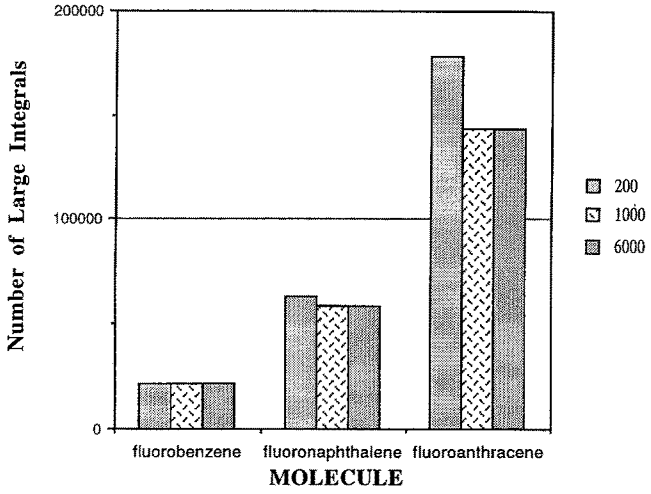

Fig. 2. Number of large contributions ($> 10^{-8}$) for fluorobenzene, fluoronaphthalene, and fluoroanthracene after 200, 1000, and 6000 2 × 2 rotations

Table 5. Number of iterations required for the convergence of the localization procedure at each quadrature point t_α of Eq. (16). Listed below are the results for fluorobenzene (FB), fluoronaphthalene (FN), and fluoroanthracene (FA), using both Boys localization and population localization schemes. The results for both occupied and virtual orbitals are reported for Boys method. Each iteration represents N 2 × 2 rotations where N is the number of orbitals that are being localized

n	Population			Boys					
	Occupied orbitals			Occupied orbitals			Virtual orbitals		
	$N = 18$ FB	$N = 27$ FN	$N = 36$ FA	$N = 18$ FB	$N = 27$ FN	$N = 36$ FA	$N = 15$ FB	$N = 24$ FN	$N = 33$ FA
1	34	46	65	417	263	229	63	85	137
2	34	46	63	414	260	221	79	92	142
3	32	54	61	339	218	177	61	95	140
4	32	47	70	202	105	147	57	90	154
5	34	51	67	72	105	136	75	70	130
6	40	57	81	67	98	417	47	108	138
7	64	93	135	63	160	372	48	102	155
8	193	253	674	157	201	> 1000	81	149	492

localization for fluorobenzene converges within 200 2 × 2 rotations for each virtual localization as compared to nearly 600 for the occupied localization. Thus the convergence behavior of this scheme is comparable to that of occupied orbital schemes, though the requirement of an individual localization for each unique pair of occupied orbitals necessitates the use of convergence cutoffs.

In Fig. 3, a comparison of the number of significant contributions in conventional MP2 to those in Laplace MP2 for the six test systems is shown. A contribution is defined as a single term in the sums (1) and (16), respectively. Clearly, the

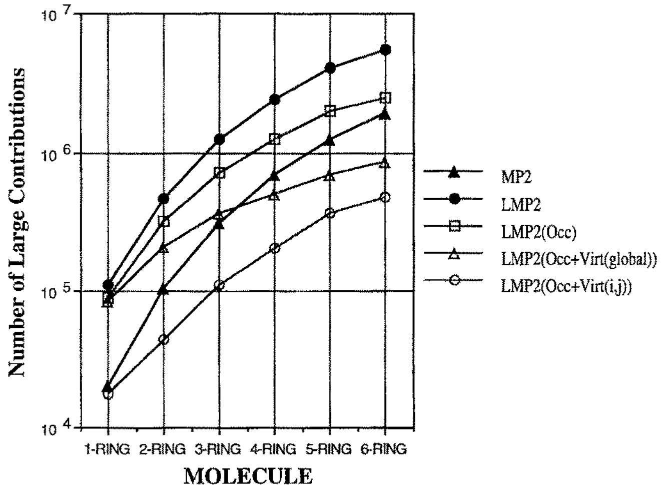

Fig. 3. The number of large contributions to the MP2 energy for Laplace MP2 with canonical orbitals (LMP2), with localized occupied orbitals (LMP2(Occ)), Laplace MP2 with globally localized occupied orbitals and virtual orbitals (LMP2(Occ + Virt(global))), and Laplace MP2 with localized occupied orbitals and virtual orbitals localized with respect to occupied orbital pairs (LMP2(Occ + Virt(i, j)). The molecules studied (1RING-6RING) are the same as in Table 4

localization of the occupied orbitals reduces the number of significant contributions, but there are still more significant contributions than for conventional MP2 due to the repeated evaluation for each quadrature point. For the larger systems, the numbers are approaching the levels for conventional MP2.

Along with the localization of the occupied space, several virtual localization schemes were used. The first of these was a Boys "global" localization of all the virtual orbitals. The results are shown in Fig. 3, along with those of the previous methods. Fluoronaphthacene is the first test system where the number of large contributions has been reduced beyond those in conventional MP2. The savings become even more substantial for larger systems as shown.

However, it is desirable to have as few large contributions as possible, so attempts were made to achieve even more substantial savings by using techniques designed to localize the virtual orbital space specifically for each occupied pair. As shown in Fig. 3, fluoronaphthalene is the first test system where this method results in fewer large integrals than conventional methods. The number of large contributions is reduced even beyond the reduction in the global virtual method. However, the results for the global virtual method approach those for the virtual localization with respect to occupied orbital pairs for fluorohexacene. There are a couple of possible reasons for this. First, a cutoff of 200 2×2 rotations was used for the virtual localization with respect to occupied orbital pairs. As shown in Table 5, the localization in the larger systems is less well converged at a fixed number of rotations. Another possibility is that localized occupied and virtual orbitals are more likely to be far apart even with a "global" localization scheme as a system size increases. Thus, the result for fluorohexacene could reflect the decreasing importance of the type of method used to localize the orbitals.

The results from the virtual localization with respect to an individual occupied orbital are somewhat surprising. Because this technique specifically addresses the differential overlaps, this method was expected to result in fewer large contributions than for the Boys localization of the virtual orbitals. This method was also expected to result in slightly more large contributions than for the localization with respect to occupied orbital pairs. As illustrated in Fig. 4, the number of large contributions for this method is less than the number for a global localization of the virtual orbitals. However, for fluoronaphthalene, using a virtual localization with respect to a single occupied orbital resulted in only approximately 3% fewer large contributions than the global localization of the virtual orbitals. Because of the additional work and additional space required for this method over that required for global localization, the latter is the much more viable option. Larger systems were not tested with this method.

From these results, it appears that the virtual localization with respect to occupied orbital pairs produces the smallest number of large contributions. Thus, the greatest reduction in storage requirements would result from this method. In practice, however, the cost of this technique is prohibitive as it does scale as N^5. If the scaling could be reduced, or if a less expensive approximation to this approach could be used, then this method would be a viable approach.

7 Integral screening

In order to make use of the sparsity provided by the localization, effective prescreening of two-electron integrals is needed. For this, an estimate of the magnitude of the transformed and untransformed integrals is necessary. There are several ways in which a four-center integral can be approximated with two-index quantities, the most powerful of which is one based on the Schwartz inequality [19]. For the present purpose, however, it is preferable to work with a simpler estimate using radial overlaps. It is straightforward to show that a four-center, two-electron integral over Gaussian basis functions can be written as [20]

$$\langle pr \mid qs \rangle = S_{pq} S_{rs} \Theta_{pqrs}, \tag{21}$$

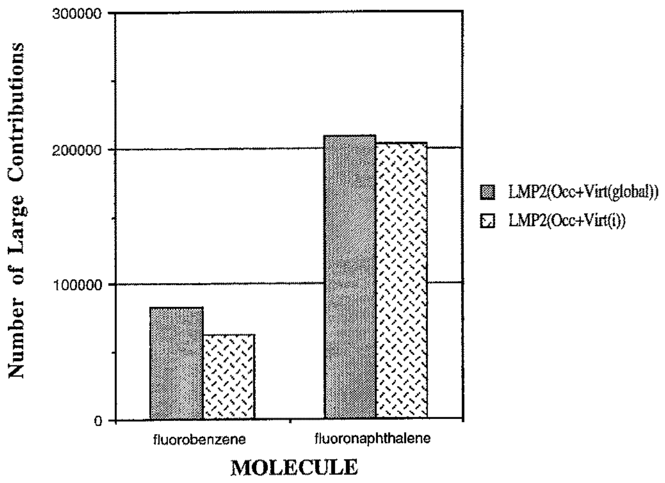

Fig. 4. A comparison of global and individual localization of virtual orbitals for fluorobenzene and fluoronaphthalene. Boys localization was used for the global localization scheme

where S_{pq} is a radial overlap between basis functions p and q, and Θ_{pqrs} is slowly varying angular factor. Approximating an AO integral in this spirit,

$$\langle pr \mid qs \rangle \approx S_{pq} S_{rs}, \tag{22}$$

the radial overlap product can be transformed exactly as the AO integral, and the various combinations of radial overlaps, partially transformed radial overlaps, and fully transformed radial overlaps can be used as test criteria. For instance, in the first step of the transformation where the AO integral $\langle pr \mid qs \rangle$ is transformed to $\langle pr \mid qj \rangle$,

$$\langle pr \mid qj \rangle = \sum_s C_{sj} \langle pr \mid qs \rangle, \tag{23}$$

the criterion on whether the $\langle pr \mid qj \rangle$ integral needs to be evaluated is given by a radial overlap multiplied by a partially transformed overlap (using absolute values of the molecular orbital coefficients)

$$\langle pr \mid qj \rangle \approx S_{pq} S_{rj}. \tag{24}$$

Such a screening criterion can also of course be used in conventional MP2, but the delocalized nature of canonical orbitals certainly would greatly limit its usefulness.

To investigate the effect of integral screening, linear chains of water molecules were used as test systems. Calculations were done on up to six water molecules separated by a distance of 5 Å, using a DZ basis. In the largest calculation, over 94% of the two-electron integrals $\langle pr \mid qj \rangle$ were eliminated with a threshold of 10^{-7}. With thresholds of 10^{-8}, 78% of both the $\langle pr \mid bj \rangle$ and the $\langle pi \mid bj \rangle$ integrals were avoided, while approximately 25% of the final $\langle ai \mid bj \rangle$ fell below a threshold of 10^{-10}. The thresholds were chosen to produce approximately the same error ($\approx 10^{-7}\ E_h$) at all levels of screening, and the different thresholds obtained reflect the fact that the errors made in the first steps contribute randomly to the error in the final total energy, whereas the $\langle ai \mid bj \rangle$ integrals contribute with a preferential sign. The average fraction of integrals eliminated in these calculations is shown in Fig. 5. The trend clearly indicates that even more substantial screening is to be expected in larger systems. However, due to the systematic nature of the error caused by the neglect of the final $\langle ai \mid bj \rangle$ integrals, it is expected that the thresholds for the last part of the transformation will have to be tightened as the size of the system increases.

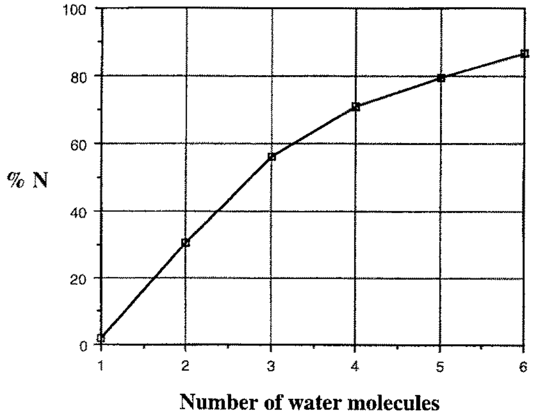

Fig. 5. Average screening in MP2 for chains of water molecules, using a DZ basis. The separation of molecules is 5 Å. The resulting energy errors are less than 0.5 μE_h. N represents the total number of partially and fully transformed two-electron integrals in the calculation

8 Conclusion

We have shown that the Laplace technique provides a means for integral reduction by removing the canonical constraint in MP2 and allowing the use of localized orbitals. This reduces the number of significant contributions to the correlation energy, thus increasing the sparsity of the integral arrays and allowing storage requirement reductions. Though extra work is required, this is more than offset by the savings in storage requirement.

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Note added in proof
A similar paper by Rauhab and Pulay was submitted to Chemical Physics Letters after our work was submitted.

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