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Cite as: J. Chem. Phys. **96**, 489 (1992); <https://doi.org/10.1063/1.462485>

Submitted: 20 August 1991 . Accepted: 26 September 1991 . Published Online: 04 June 1998

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Laplace transform techniques in Møller–Plesset perturbation theory

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(Received 20 August 1991; accepted 26 September 1991)

We discuss how the computational obstacles related to energy denominators in various schemes for electron-correlation calculations can be circumvented by a Laplace transform technique. The method is applicable to a wide variety of electronic structure calculations. We discuss in detail an algorithm for the contribution of triple excitations in fourth-order Møller–Plesset perturbation theory, which grows only with the sixth power of the size of the system, as compared to conventional N^7 algorithms. Special consideration is given to efficient schemes for numerical quadrature of the integrals occurring in the Laplace transformations.

I. INTRODUCTION

Recent development of direct methods for electronic structure calculations^{1–4} has allowed the application of rigorous *ab initio* theory to molecules of a size which was unthinkable only few years ago. Self-consistent field (SCF) calculations are now possible on systems with nearly 2000 basis functions^{5,6} and, even at the correlated level, very large basis sets are routinely being used.^{7,8} However, these correlated methods generally show a steep power-law dependence on the size of the system or, more precisely, on the dimensionality of the occupied and virtual spaces used in the correlation treatment. In a previous paper⁹ we have used a Laplace transform to eliminate the energy denominators in perturbation theory, lifting the constraint of canonical orbitals. In a spin-orbital formalism, the second-order correction to the electronic energy can be written as

$$E^{(2)} = -\frac{1}{4} \sum_{ijab} \frac{\langle ab || ij \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (1a)$$

$$= -\frac{1}{4} \int_0^\infty dt \sum_{ijab} \langle ab || ij \rangle^2 e^{-(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t} \quad (1b)$$

$$= \int_0^\infty e^{(2)}(t) dt, \quad (1c)$$

where

$$e^{(2)}(t) = -\frac{1}{4} \sum_{ijab} \langle a(t)b(t) || i(t)j(t) \rangle^2 \quad (2)$$

and

$$\psi_i(t) = \psi_i(0) e^{\epsilon_i t/2}, \quad (3a)$$

$$\psi_a(t) = \psi_a(0) e^{-\epsilon_a t/2}. \quad (3b)$$

As usual, the indices i, j, k, \dots denote occupied orbitals, a, b, c, \dots denote virtuals, and the double-bar bracket $\langle pq || rs \rangle$ is a shorthand notation for the combination of integrals,

$$\langle pq || rs \rangle = \langle pq | rs \rangle - \langle pq | sr \rangle = \langle pr | qs \rangle - \langle ps | qr \rangle. \quad (4)$$

At the expense of evaluating the integral (1c), which can be accomplished by any conventional numerical quadrature scheme, the energy denominators are eliminated and, hence, the requirement of canonical orbitals is lifted. The function $e^{(2)}(t)$ is quite well behaved and monotonically decreasing, and this integration is not a major computational obstacle.

In this work we show that, with a suitable choice of quadrature points (see below) fewer than 10 points are required for 6–7 digits of accuracy, which is usually sufficient to obtain correlation energies within a micro-hartree. Especially with localized orbitals in extended systems, the price paid for the repeated evaluation of $e^{(2)}(t)$ at different values of t is more than offset by the much smaller effective orbital spaces needed in a localized scheme.^{10,11} The exponential factors in Eq. (3) will effectively eliminate all but the highest occupied and lowest virtual orbitals for large values of t . Accordingly, the quadrature points corresponding to large t values will be relatively inexpensive with a reasonable screening to eliminate numerically insignificant contributions. It is also worth noting that the contributions for different quadrature points can be evaluated in parallel, and the scheme is therefore well suited for many modern, high-performance computer architectures.

In this work we demonstrate that a similar technique can be used to effectively decouple the nested summations in higher-order perturbation theory, allowing for independent partial summations and a lower overall power dependence on the basis set size. We illustrate the technique with an application to the contributions from triple excitations in fourth-order Møller–Plesset perturbation theory.

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II. PERTURBATION THEORY

In fourth-order Møller–Plesset perturbation theory, the most time-consuming contributions to the total energy are of the form,

$$E_{\mu}^{(4)} = \sum_{\nu}^{\prime} \sum_{\tau}^{\prime} \sum_{\sigma}^{\prime} \frac{\langle \Psi_{\mu} | V | \Psi_{\nu} \rangle \langle \Psi_{\nu} | V | \Psi_{\tau} \rangle \langle \Psi_{\tau} | V | \Psi_{\sigma} \rangle \langle \Psi_{\sigma} | V | \Psi_{\mu} \rangle}{(E_{\mu}^{(0)} - E_{\nu}^{(0)}) (E_{\mu}^{(0)} - E_{\tau}^{(0)}) (E_{\mu}^{(0)} - E_{\sigma}^{(0)})} \quad (5)$$

Ψ_{ν} and Ψ_{σ} are doubly excited with respect to the reference state Ψ_{μ} , whereas Ψ_{τ} can be singly, doubly, triply, or quadruply excited. In Møller–Plesset perturbation theory, the sums over k -tuply excited states are replaced by $2k$ -fold summations over orbitals, and the energy differences in the denominators are expressed as orbital energy differences. For the most general contributions, expressions involving up to $2M$ orbitals occur in M th order of Møller–Plesset (MP) perturbation theory.

To illustrate the Laplace integration technique, we consider one typical expression for the MP4 triples contribution to the MP4 energy of the form^{12–14}

$$\Delta E^{(4)}(T) = \sum_{ijklcde} \frac{\langle ij || ab \rangle \langle ak || cd \rangle \langle cb || ek \rangle \langle ed || ij \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)(\epsilon_b + \epsilon_c + \epsilon_d - \epsilon_i - \epsilon_j - \epsilon_k)(\epsilon_d + \epsilon_e - \epsilon_i - \epsilon_j)} \quad (6)$$

Introducing the usual notation

$$C_{ijab}^{(1)} = \frac{\langle ij || ab \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)} \quad (7)$$

along with a Laplace transform for the remaining denominator in (6), we obtain

$$\int_0^{\infty} \sum_{ijklcde} C_{ijab}^{(1)} \langle ak || cd \rangle \langle cb || ek \rangle \times C_{ijde}^{(1)} e^{-t[(\epsilon_d - \epsilon_i - \epsilon_j) + (\epsilon_b + \epsilon_c - \epsilon_k)]} dt \quad (8)$$

By introducing the auxiliary matrices

$$X_{ab,de}(t) = \sum_{ij} C_{ijab}^{(1)} C_{ijde}^{(1)} e^{-(\epsilon_d - \epsilon_i - \epsilon_j)t} \quad (9)$$

and

$$Y_{de,ab}(t) = \sum_{kc} \langle ak || cd \rangle \langle cb || ek \rangle e^{-(\epsilon_b + \epsilon_c - \epsilon_k)t}, \quad (10)$$

the expression for the energy contribution under consideration takes the form

$$\Delta E^{(4)}(T) = \int_0^{\infty} \text{Tr}\{X(t)Y(t)\} dt \quad (11)$$

The evaluation of the trace is a N^4 procedure (actually N_v^4 where N_v is the number of virtual orbitals). The number of elements to be evaluated in each of the matrices X and Y is also of the order N_v^4 . Since each of the matrix elements of Y require $N_0 N_v$ operations, a straightforward implementation amounts to of the order $N_0 N_v^5$ steps. Other contributions to the MP4(T) energy can be evaluated in a similar fashion.

A similar analysis can be applied to all terms occurring in the perturbation expansion. In particular, those contributions in fourth-order perturbation theory which would require a n^7 procedure with a conventional summation can all be written in the form

$$\int_0^{\infty} \sum_{*****} C_{*****}^{(1)} \langle ** || ** \rangle \langle ** || ** \rangle C_{*****}^{(1)} e^{-t\Delta\epsilon} dt, \quad (12)$$

where an asterisk (*) denotes an unspecified (i.e., occupied

or virtual) molecular orbital index. When the exponential is factored and incorporated into the first-order coefficients and/or the integrals, the time-critical part of the calculation reduces to a straight summation of four four-index quantities. As each index occurs twice, it can be seen from simple topological considerations that there must always be two four-index objects having at least two indices in common. These can now be contracted using a procedure no more expensive than N^6 , which would therefore be the rate-determining step of the summation. The entire summation can therefore be carried out at the N^6 level with a storage requirement no worse than N^4 . For large systems this would compare favorably to the usual $N_0^3 N_v^4$ dependence of conventional schemes, if the numerical quadrature of Eq. (11) can be carried out efficiently. That problem will be addressed in Sec. III.

It also deserves to be mentioned in this context, that the aforementioned technique applies equally well to higher orders of Møller–Plesset perturbation theory. The usual, high power dependence of conventional schemes on the number of orbitals stems at least partly from the occurrence of nonseparable factors in the energy denominators. Generally, up to M -tuply excited states (M even) occur in expressions for the correlation energy in M th and $(M + 1)$ th order of perturbation theory; the nonseparable factors in the denominators may therefore contain up to $2M$ different orbitals indices, and the computational requirement for M th order perturbation theory will typically grow by at least 1 order for every order of perturbation theory. Relations exist¹² which reduce this power dependence in special cases (e.g., quadruple excitations in MP4 which can be accounted for at an expense no worse than N^6), but no such techniques are known for the general case. With the Laplace transform, the offending factors in the denominators can always be transferred into multiple quadrature schemes. In higher orders, there will be cases which require combination of four-index quantities with only one index in common, and the N^6 dependence discussed above for MP4 can no longer be achieved. In these cases, the computational requirements will instead grow as

$N^8 m^{M-3}$ for $M = 5, 6$, and 7 , where m is the number of quadrature points required for the Laplace integration and M is the order of perturbation theory.

III. THE NUMERICAL QUADRATURE

A successful utilization of the Laplace transform in quantum-chemical calculations hinges on an efficient and generally applicable scheme for evaluating the Laplace integral numerically. In this section we devise such a scheme, and demonstrate its performance for the special but important case of MP2 calculations.

The basic idea of all Laplace MP n schemes is to replace undesirable denominators (sums and differences of orbital energies) by their Laplace transforms which allow a factorization of terms. If x_q is such a denominator, e.g., in MP2 $x_q = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$, where q serves as a collective index for (a, b, i, j) , we would thus replace

$$\frac{1}{x_q} \approx \int_0^\infty dt e^{-x_q t}, \quad (13)$$

which holds for all $x_q > 0$. To carry out the Laplace integration numerically amounts to replacing the integral in Eq. (13) by a finite sum,

$$\frac{1}{x_q} = \sum_{\alpha=1}^{\tau} w_{\alpha} e^{-x_q t_{\alpha}}. \quad (14)$$

This formula may also be interpreted as an approximation of the function $1/x$ by a superposition of exponential functions $\exp(-xt_{\alpha})$ with weights (fit coefficients) w_{α} . The aim is to determine the weights w_{α} and the exponential factors t_{α} which reproduce $1/x$ most accurately for all occurring values x_q .

We have chosen to accomplish this task by a least-squares approximation,

$$\sum_q f_q \left(\frac{1}{x_q} - \sum_{\alpha=1}^{\tau} w_{\alpha} e^{-x_q t_{\alpha}} \right)^2 = \min!, \quad (15)$$

where (in MP2) q runs over all molecular orbital (MO) index quadruples (a, b, i, j) . In this formula we have introduced (positive) weights f_q for the least-squares procedure. For an MP2 scheme the best weights would obviously be $f_q = \langle ab || ij \rangle^2$. It is one of the many virtues of the Laplace MP n technique; however, it is possible to avoid two-electron MO integrals altogether, by a "direct" construction of the two-electron density in other (nonorthogonal) basis sets. It is therefore advantageous to avoid two-electron MO integrals also in the least-squares approximation which must precede the actual calculation of the correlation energy. There are many possibilities to obtain upper bounds for expressions like $\langle ab || ij \rangle^2$.¹⁵⁻¹⁸ It turns out, however, that the least-squares approximation is not overly sensitive to changes in the weights f_q : Setting $f_q = 1$ for all $q = (a, b, i, j)$ already yields an approximation useful in actual Laplace MP2 calculations.

An apparent disadvantage of the least-squares condition, Eq. (15), is that it involves a summation over q (orbital quadruples in MP2). This shortcoming can be addressed by replacing the explicit summation over index quadruples q by

an integral over the interval $[\min(x_q), \max(x_q)]$ with a weight function $f(x) \geq 0$ which simply counts the number of x_q in the vicinity of x . Equation (15) then reads as

$$\int_{x_{\min}}^{x_{\max}} dx f(x) \left(\frac{1}{x} - \sum_{\alpha=1}^{\tau} w_{\alpha} e^{-x t_{\alpha}} \right)^2 = \min!. \quad (16)$$

In our implementation of the least-squares procedure, the x integration is carried out with a midpoint formula applied to about 1200 subintervals ranging in length from 0.004 at $x = 0.75$ to 1.8 at $x = 360$ (a logarithmic grid was used). The evaluation of $f(x)$ can be accomplished by an N^2 procedure.

The integrals occurring in Eq. (16) can be obtained analytically [yielding terms containing the exponential integral function $E_1(z)$] if $f(x)$ is set to unity over the entire interval. This constitutes the simplest solution to the approximation problem.

Regardless as to how $f(x)$ is chosen, it is always possible to calculate the least-squares integral, Eq. (16), and various derivatives of it with respect to the parameters w_{α} and t_{α} at a comparatively small cost. The weights w_{α} , in particular, can be obtained for any choice of the exponential factors t_{α} by solving the system of linear equations

$$\mathbf{B} \mathbf{w} = \mathbf{a}, \quad (17)$$

where

$$\mathbf{a}_{\alpha} = \int_{x_{\min}}^{x_{\max}} dx f(x) \frac{1}{x} e^{-x t_{\alpha}}, \quad (18)$$

$$\mathbf{B}_{\alpha\beta} = \int_{x_{\min}}^{x_{\max}} dx f(x) e^{-x(t_{\alpha} + t_{\beta})}, \quad (19)$$

and \mathbf{B} is a symmetric and positive definite matrix. Differentiation of Eq. (16) with respect to t_{α} yields an independent set of similar equations.

Unfortunately, however, the condition number of \mathbf{B} and of related matrices grows exponentially as the number τ of exponentials increases and, for $\tau \geq 5$, round-off errors can impede an accurate solution of the nonlinear equations for the exponential factors t_{α} .

To find the optimal exponential factors t_{α} , we have used the numerically very robust Simplex algorithm, applied directly to the least-squares condition Eq. (16) with the weights w_{α} determined from Eq. (17). In all examples studied so far, the optimum weights w_{α} and exponential factors t_{α} are found to be positive. We have applied the technique to the evaluation of the MP2 energy integral, Eq. (1c), according to

$$E_{\text{MP2}}^{(\tau)} = -\frac{1}{4} \sum_{\alpha=1}^{\tau} \sum_{ij,ab} \langle a_{\alpha} b_{\alpha} || i_{\alpha} j_{\alpha} \rangle^2, \quad (20)$$

where

$$|i_{\alpha}\rangle = \psi_i(t_{\alpha}) = w_{\alpha}^{1/8} \psi_i(0) e^{(\epsilon_i + \epsilon_F) t_{\alpha}/2}, \quad (21a)$$

$$|a_{\alpha}\rangle = \psi_a(t_{\alpha}) = w_{\alpha}^{1/8} \psi_a(0) e^{(\epsilon_F - \epsilon_a) t_{\alpha}/2}, \quad (21b)$$

ϵ_i and ϵ_a are the orbital energies of the MOs i and a , respectively, and ϵ_F is any value chosen to lie in the HOMO-LUMO interval. The introduction of ϵ_F is merely a

TABLE I. Exponential coefficients t_α and weights w_α (second set of numbers in each group) for the least-squares approximation of $1/x$ by a varying number (τ) of exponentials $\exp(-xt_\alpha)$ for a calculation of the all-valence MP2 energy of C_3H_4CIP .

$\alpha =$	1	2	3	4	5	6	7	8
τ								
1	0.254 306 6 0.744 377 8							
2	0.105 737 4 0.299 852 9	0.826 398 5 1.375 040 4						
3	0.066 461 8 0.179 391 9	0.438 078 5 0.632 960 2	1.610 192 5 1.999 684 8					
4	0.013 596 7 0.052 717 1	0.164 637 4 0.275 764 7	0.656 970 2 0.785 802 4	2.035 781 5 2.278 667 9				
5	0.006 478 5 0.017 780 6	0.066 915 4 0.127 850 0	0.308 915 6 0.387 837 5	0.947 880 8 0.974 109 8	2.578 639 3 2.612 573 2			
6	0.006 005 0 0.016 442 1	0.055 301 6 0.099 569 4	0.234 650 0 0.275 945 8	0.658 778 1 0.610 680 6	1.576 060 6 1.317 866 4	3.650 257 5 3.185 700 8		
7	0.003 524 3 0.009 590 4	0.025 193 9 0.043 706 2	0.119 358 3 0.156 652 8	0.365 393 6 0.354 293 7	0.885 052 6 0.726 452 8	1.945 461 7 1.492 883 6	4.240 146 8 3.463 434 8	
8	0.003 425 0 0.009 303 5	0.023 862 7 0.039 002 2	0.102 343 0 0.126 746 5	0.294 735 9 0.269 294 5	0.673 604 6 0.511 299 3	1.382 183 7 0.951 267 3	2.713 349 7 1.816 383 5	5.405 109 0 3.952 214 6

matter of numerical convenience, and guarantees that the exponentials have a negative argument.

As an illustrative medium-sized test molecule, we have chosen *p*-chloro-phospha-benzene C_3H_4CIP which has C_{2v} symmetry. The Laplace MP2 calculations were performed with a $(8s4p1d;4s1p;11s6p1d;11s6p1d)/[4s2p1d;2s1p;5s4p1d;5s4p1d]$ basis set¹⁹ with the core orbitals frozen. The molecular geometry was obtained from a geometry optimization at the SCF level of theory with the same basis set. The SCF energy is -991.802781 a.u. The second-order correlation energy (as evaluated by conventional methods) is -0.911294 a.u. The eigenvalues of the highest and lowest occupied valence orbitals are -0.3238 and -1.1938 a.u., respectively; the eigenvalue of the lowest virtual orbital is $+0.0626$ a.u. There are two very high lying virtual orbitals at $+135.25$ and $+177.40$ a.u.; their elimination reduces the (conventional) MP2 energy by 7 microhartree to -0.911287 .

Table I shows the exponential coefficients t_α and weights w_α as calculated from Eq. (15) for up to eight exponential functions $\exp(-xt_\alpha)$ approximating $1/x$ in the interval $(x_{\min}, x_{\max}) = (0.77, 358.1)$, with the weight function $f(x)$ counting the number of orbital energy differences $x_q = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$ in the vicinity of x .

Table II gives the corresponding Laplace MP2 energies $E_{MP2}^{(\tau)}$ as obtained with τ exponentials approximating $1/x$. The relative error is compared to two simple precomputed error estimates $L1$ and $L2$, defined as

$$L1 = \int f(x) \left| \frac{1}{x} - \sum_{\alpha=1}^{\tau} w_\alpha e^{-xt_\alpha} \right| dx \int \frac{f(x)}{x} dx \quad (22)$$

and

$$L2 = \left(\int f(x) \left| \frac{1}{x} - \sum_{\alpha=1}^{\tau} w_\alpha e^{-xt_\alpha} \right|^2 dx \right)^{1/2} \times \left(\int f(x) dx \right)^{1/2} \left(\int \frac{f(x)}{x} dx \right). \quad (23)$$

Table II shows that micro-hartree accuracy can be obtained with eight terms in the expansion of $1/x$. Both error estimates $L1$ and $L2$ appear to provide a reliable estimate of the actual relative error.

If the two highest virtual orbitals are frozen, the interval (x_{\min}, x_{\max}) shrinks to $(0.77, 27.4)$, and the exponential approximation of $1/x$ should become simpler in terms of the number of exponentials needed. This is demonstrated in Table III where the results of the Laplace MP2 calculation for this system are shown. For a given requirement of accuracy, one exponential term less is needed, compared to when the two highest virtual orbitals were included.

All of these results were obtained with the least-squares

TABLE II. All-valence Laplace MP2 energies $E_{MP2}^{(\tau)}$ of C_3H_4CIP according to Eq. (19), relative errors, and error estimates $L1$ and $L2$. Exponential coefficients t_α and weights w_α as given in Table I. The correct MP2 energy is -0.911294 .

τ	$E_{MP2}^{(\tau)}$	Rel. error	$L1$	$L2$
1	-0.871 901	4.3E-2	9.9E-2	1.4E-1
2	-0.905 636	6.2E-3	1.5E-2	2.1E-2
3	-0.909 917	1.5E-3	2.9E-3	6.4E-3
4	-0.910 740	6.4E-4	9.3E-4	1.5E-3
5	-0.911 080	2.3E-4	2.8E-4	4.2E-4
6	-0.911 254	4.4E-5	4.5E-5	8.8E-5
7	-0.911 282	1.3E-5	1.5E-5	2.3E-5
8	-0.911 293	1.5E-6	2.7E-6	5.5E-6

TABLE III. All-valence Laplace MP2 energies $E_{\text{MP2}}^{(\tau)}$ of $\text{C}_5\text{H}_4\text{ClIP}$ with the two highest virtual orbitals frozen, relative errors, and the error estimates $L1$ and $L2$. The correct MP2 energy is -0.911287 .

τ	$E_{\text{MP2}}^{(\tau)}$	Rel. error	$L1$	$L2$
1	-0.871809	4.3E-2	9.8E-2	1.3E-1
2	-0.905634	6.2E-3	1.4E-2	2.0E-2
3	-0.909923	1.5E-3	1.9E-3	3.0E-3
4	-0.911044	2.7E-4	3.2E-4	4.8E-4
5	-0.911241	5.0E-5	4.7E-5	7.2E-5
6	-0.911282	5.5E-6	7.0E-6	1.1E-5
7	-0.911286	0.7E-6	1.0E-6	1.5E-6

weight function $f(x)$ derived from the distribution of the MP2 energy denominators x_q . We also studied the simpler weight function $f(x) = 1$ for all $x \in (x_{\min}, x_{\max})$. Results for the all-valence Laplace MP2 calculation on $\text{C}_5\text{H}_4\text{ClIP}$ and this weight function are given in Table IV (no frozen virtual orbitals). At first glance the relative errors appear to be very similar to those in Table II, but closer inspection reveals three important differences. (1) The Laplace MP2 energies oscillate around the “exact” MP2 energy. (2) The absolute values of the errors fluctuate, and are up to 3 times larger than the relative errors in Table II. (3) $L1$ and $L2$ now overestimate the actual relative errors significantly.

All three observations are consistent with the notion that errors derived from the least-squares approximation of $1/x$ with a constant weight function $f(x) = 1$ behave predominantly as statistical errors, whereas a systematic error dominates when $f(x)$ is derived from the distribution of orbital energy differences x_q . The systematic underestimation of MP2 energies in Table II may be traced to the neglect of the MO integral size distribution over x . The largest MO integrals usually occur for smaller values of x_q , where the approximating function

$$\sum_{\alpha} \omega_{\alpha} \exp(-x t_{\alpha})$$

is smaller than $1/x$ according to their limiting behavior as $x \rightarrow 0$. Accordingly, the contributions of the highest occupied

and lowest unoccupied molecular orbitals will be systematically underestimated. This will not happen to the same degree if the constant least-squares weight function $f(x) = 1$ is used, since it gives a relatively larger weight to the tails of the spectrum.

We conclude that the approximation of MP2 orbital energy denominators by a sum of exponentials, Eq. (15), can be achieved with micro-hartree accuracy using only about eight terms. Further improvement seems possible if an empirically established integral size distribution is incorporated into the least-squares weight function $f(x)$. Note that it suffices to establish the size distribution of two-index two-electron integrals like $\langle ia|ia \rangle$ over $\epsilon_a - \epsilon_i$, since it can be shown that

$$\langle ab||ij \rangle^2 + \langle ab||ji \rangle^2 \leq 3(\langle aa||ii \rangle \langle bb||jj \rangle + \langle aa||jj \rangle \langle bb||ii \rangle). \quad (24)$$

With regard to the approximation of the six-orbital energy denominators in the MP4(T) expression we note that a smaller relative accuracy is sufficient for micro-hartree accuracy, since the absolute magnitude of the MP4 triples contribution amounts to only a few percent of the total correlation energy.¹⁴

IV. SUMMARY

We have shown that the discrete Laplace method is a feasible technique to eliminate energy denominators in perturbation calculations of electron correlation. While several methods involving Laplace transforms are well known in diagrammatic perturbation theory (see, e.g., Refs. 20 and 21), the technique to reduce the computational cost of high-order perturbation theory by a factorization of denominators appears to be new. Several computational simplifications are possible once the explicit denominators are disposed of. It was previously shown that the modified MP2 energy expression is invariant to orbital rotations, and a localization of orbitals is therefore possible.⁹ That scheme provides an interesting alternative to other local correlation methods,^{10,11} and allows the direct construction of an MP2 two-particle density in a nonorthogonal basis set without prior calculation of two-electron MO integrals. Further-

TABLE IV. All-valence Laplace MP2 energies $E_{\text{MP2}}^{(\tau)}$ of $\text{C}_5\text{H}_4\text{ClIP}$ with least-squares weight function $f(x)$ set to 1 in $(x_{\min}, x_{\max}) = (0.77, 358.1)$. The error estimates $L1'$ and $L2'$ were obtained with the weight function $f(x) = 1$, whereas $L1$ and $L2$ pertain to a weight function derived from the density distribution of $x_q = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j$. The correct MP2 energy is -0.911294 .

τ	$E_{\text{MP2}}^{(\tau)}$	Rel. error	$L1'$	$L2'$	$L1$	$L2$
1	-0.857659	5.9E-2	2.1E-1	2.7E-1	2.9E-1	3.3E-1
2	-0.895468	1.7E-2	5.9E-2	6.8E-2	4.9E-2	5.6E-2
3	-0.914435	-3.4E-3	1.9E-2	2.1E-2	1.6E-2	1.8E-2
4	-0.911625	-3.6E-4	6.3E-3	7.1E-3	5.6E-3	6.2E-3
5	-0.911208	9.4E-5	1.9E-3	2.2E-3	1.6E-3	1.9E-3
6	-0.911270	2.6E-5	5.6E-4	6.4E-4	5.1E-4	5.7E-4
7	-0.911294	<1.0E-6	1.6E-4	1.9E-4	1.5E-4	1.7E-4
8	-0.911298	-4.4E-6	4.7E-5	5.4E-5	4.4E-5	4.9E-5

more, removing the denominators, as well as lifting the constraints of canonical orbitals, is an advantage for the construction of derivatives of the energy with respect to various perturbations. In higher-order perturbation theories, the elimination (full or in part) of denominators leads to a reduced N dependence. Indeed, it is possible to apply the Laplace technique to obtain new expressions for the inverse of definite operators of the form $(A - B)^{-1}$ which occur in infinite order perturbation theory.²² To carry out these calculations in a computationally efficient way, we have devised a numerical quadrature scheme requiring fewer than ten terms to obtain micro-hartree accuracy.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation, Grant No. CHE-8915629, and by the Deutscher Akademischer Austauschdienst (DAAD).

¹ J. Almlöf, K. Faegri, and K. Korsell, *J. Comput. Chem.* **3**, 385 (1982).

² R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).

³ S. Saebø and J. Almlöf, *Chem. Phys. Lett.* **154**, 83 (1989).

⁴ M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chem. Phys. Lett.* **153**, 503 (1988).

⁵ J. Almlöf and H. P. Lüthi, *A.C.S. Symposium Series 353: Supercomputer Research in Chemistry and Chemical Engineering* (American Chemical Society, Washington, D.C., 1987), p. 35

⁶ G. Scuseria, *Chem. Phys. Lett.* **176**, 423 (1991).

⁷ M. Häser, J. Almlöf, and G. Scuseria, *Chem. Phys. Lett.* **181**, 497 (1991).

⁸ V. Parasuk, J. Almlöf, and M. W. Feyereisen, *J. Am. Chem. Soc.* **113**, 1049 (1991).

⁹ J. Almlöf, *Chem. Phys. Lett.* **176**, 319 (1991).

¹⁰ P. Pulay and S. Saebø, *Theor. Chim. Acta* **69**, 357 (1986).

¹¹ S. Saebø and P. Pulay, *J. Chem. Phys.* **86**, 914 (1987); **88**, 1884 (1988).

¹² G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **68**, 2114 (1978).

¹³ R. J. Bartlett and G. D. Purvis, *Int. J. Quantum Chem.* **14**, 561 (1978).

¹⁴ R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980).

¹⁵ J. L. Whitten, *J. Chem. Phys.* **68**, 4496 (1973).

¹⁶ J. D. Power and R. M. Pitzer, *Chem. Phys. Lett.* **24**, 478 (1974).

¹⁷ M. Häser and R. Ahlrichs, *J. Comput. Chem.* **10**, 104 (1989).

¹⁸ S. R. Gadre, S. A. Kulkarni, and P. K. Pathak, *J. Chem. Phys.* **91**, 3596 (1989).

¹⁹ S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

²⁰ R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (McGraw-Hill, New York, 1976).

²¹ J. Paldus and J. Cizek, *Adv. Quantum Chem.* **9**, 105 (1975).

²² P.-O. Löwdin, *J. Math. Phys.* **3**, 969 (1962).