Minimax approximation for the decomposition of energy denominators in Laplace-transformed Møller–Plesset perturbation theories

Akio Takatsuka,[1,2] Seiichiro Ten-no,[1,2,a)] and Wolfgang Hackbusch[3]

[1]*Graduate School of Information Science, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan*
[2]*CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*
[3]*Max-Planck-Institute for Mathematics in the Sciences, Inselstr. 22-26, 04103 Leipzig, Germany*

We implement the minimax approximation for the decomposition of energy denominators in Laplace-transformed Møller–Plesset perturbation theories. The best approximation is defined by minimizing the Chebyshev norm of the quadrature error. The application to the Laplace-transformed second order perturbation theory clearly shows that the present method is much more accurate than other numerical quadratures. It is also shown that the error in the energy decays almost exponentially with respect to the number of quadrature points. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2958921]

I. INTRODUCTION

Development of fast correlated methods with low order scaling of computational cost is significantly important in quantum chemistry to widen the realm of the applicability of accurate electronic structure calculations. The short-range nature of electron correlation can be exploited in many-body perturbation theory by the use of localized molecular orbitals.[1] Nevertheless, we have to pay the price of abandoning the simple form of energy denominators of the canonical orbitals in these class of methods.

In the Laplace-transformed technique introduced by Almlöf,[2] the energy denominators are broken up by the transformation,

$$\frac{1}{\varepsilon_a + \varepsilon_b + \cdots - \varepsilon_j - \varepsilon_i} \int_0^\infty e^{-s(\varepsilon_a+\varepsilon_b+\cdots-\varepsilon_j-\varepsilon_i)} ds, \tag{1.1}$$

where the indices, $i, j, \ldots$, and $a, b, \ldots$, denote occupied and virtual orbitals, respectively. This ansatz has been used in many places such as Møller–Plesset second order perturbation theory (MP2),[2–5] computation of connected triples contribution in Møller–Plesset fourth order perturbation theory,[3] atomic orbital (AO)-MP2,[4,6,7] AO-MP2 energy gradient,[4,8] combinations with the resolution of the identity,[9,10] and the density-matrix-based MP2.[11,12] The Laplace-transformed technique would be useful if the number of quadrature points for the numerical integration is less than the number of cycles in iterative methods. Häser and Almlöf indeed suggested an accurate quadrature minimizing the error in the MP2 energy denominators directly.[3] The scaling of computational cost for the parameters is, however, unfavorable. Moreover, the quadrature should be constructed systematically for well-defined approximations.

In this paper, we introduce the minimax approximation in the Laplace-transformed electronic structure theory. In the following section, we outline the theory and implementation. We assess the method for Laplace-transformed MP2 energies of various closed-shell molecules in Sec. III. A summary is given in Sec. IV.

II. THEORY

The Laplace transform of a reciprocal $1/x$ in a certain interval $x \in [1, R]$ can be approximated by a numerical quadrature,

$$\frac{1}{x} \simeq E_k(x; \{\omega_\nu\}, \{\alpha_\nu\}) = \sum_{\nu=1}^k \omega_\nu \exp(-\alpha_\nu x), \tag{2.1}$$

with the roots $\{\alpha_\nu\}$ and weights $\{\omega_\nu\}$. The multiplication of $1/A$ gives the corresponding approximation in an arbitrary interval $y = Ax \in [A, B]$ with $B = AR$ as

$$\frac{1}{y} \simeq E_k(y; \{\bar\omega_\nu\}, \{\bar\alpha_\nu\}), \tag{2.2}$$

$$\bar\omega_\nu = \omega_\nu/A, \tag{2.3}$$

$$\bar\alpha_\nu = \alpha_\nu/A. \tag{2.4}$$

It is well known that there is a unique sum (2.1) minimizing the Chebyshev norm.[13] The minimax approximation in the semi-infinite range $[1, \infty)$ was also studied by Braess and Hackbusch.[14] The main features of the approximation is summarized in the following.

In the error distribution function,

$$\eta_k(x; \{\omega_\nu\}, \{\alpha_\nu\}) = E_k(x; \{\omega_\nu\}, \{\alpha_\nu\}) - \frac{1}{x}, \tag{2.5}$$

---

if there exist $2k+1$ points $(1 \le x_0 < x_1 < \cdots < x_{2k} \le R)$ fulfilling

$$\text{sign}[\eta_k(x_i, \{\omega_\nu\}, \{\alpha_\nu\})] = -\text{sign}[\eta_k(x_{i+1}, \{\omega_\nu\}, \{\alpha_\nu\})],$$

$$\forall 0 \le i \le 2k-1, \tag{2.6}$$

the set of points is called an *alternant*. By using the maximum or Chebyshev norm of the distribution function in the interval,

$$\delta_{k,[1,R]}(\{\omega_\nu\}, \{\alpha_\nu\}) = \max_{x \in [1,R]} |\eta_k(x, \{\omega_\nu\}, \{\alpha_\nu\})|, \tag{2.7}$$

the best possible approximation, $E_k(x, \{\omega_k^*\}, \{\alpha_k^*\})$, is obtained by minimizing the norm with respect to the variation of the parameters,

$$\delta_{k,[1,R]}(\{\omega_\nu^*\}, \{\alpha_\nu^*\}) \le \delta_{k,[1,R]}(\{\omega_\nu\}, \{\alpha_\nu\}), \quad \forall \{\omega_\nu\}, \{\alpha_\nu\}. \tag{2.8}$$

This is known to be the minimax approximation.[13] According to the *alternation theorem* of Chebyshev, there exist unique $2k+1$ extremum points $(1 = x_0' < x_1' < \cdots < x_{2k}' = R^*)$, which satisfy

$$\eta_k(x_i', \{\omega_\nu^*\}, \{a_\nu^*\}) = (-1)^i \delta_{k,[1,R]}(\{\omega_\nu^*\}, \{\alpha_\nu^*\}). \tag{2.9}$$

Further there is a number R^* that does not exceed a critical value R_k intrinsic for each k,

$$R^* = \min(R, R_k). \tag{2.10}$$

If $R > R_k$, the error $\eta_k(x_i', \{\omega_\nu^*\}, \{\alpha_\nu^*\})$ becomes smaller than the maximum norm $\delta_{k,[1,R]}(\{\omega_\nu^*\}, \{\alpha_\nu^*\})$ in the semi-infinite interval $[1, \infty)$. Consequently, all minimax approximations are identical for $R > R_k$. Elimination of $\delta_{k,[1,R]}$ in Eq. (2.9) gives

$$\eta_k(x_i', \{\omega_\nu^*\}, \{\alpha_\nu^*\}) + \eta_k(x_{i+1}', \{\omega_\nu^*\}, \{\alpha_\nu^*\}) = 0,$$

$$\forall 0 \le i \le 2k-1. \tag{2.11}$$

It is noted that the maximum norm of the minimax approximation decays exponentially with respect to k.[14]

The application of the alternation theorem leads to the Remez algorithm for the best approximation of $E_k(x, \{\omega_k^*\}, \{\alpha_k^*\})$. What follows is the procedure for the quadrature implemented in this work.

(1) If $R > R_k$, skip the optimization and use the parameters for R_k. Otherwise, we calculate $2k-1$ extremum points $\{x_i'\}$ except for $x_0' = 1$ and $x_{2k}' = R$ in the initial function $E_k(x, \{\omega_k\}, \{\alpha_k\})$ of pretabulated parameters. They should form an alternant.
(2) Optimize the parameters $\{\omega_k\}$ and $\{\alpha_k\}$ in such a way that Eq. (2.11) is satisfied.
(3) Find the nodal points of the solutions of $\eta_k(x_i^0, \{\omega_\nu\}, \{\alpha_\nu\}) = 0$, $(i = 1, \ldots, 2k)$, which are necessary to compose an alternant to define the intervals $I_i = [x_i^0, x_{i+1}^0]$, $(i = 1, \ldots, 2k-1)$.
(4) Compute the extremum points $\{x_i'\}$ in the intervals.
(5) Check the convergence using Eq. (2.11). If the residual
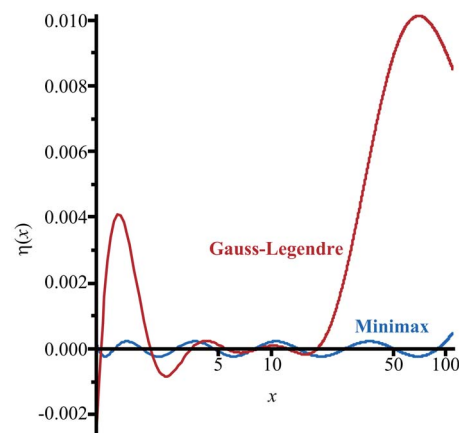

FIG. 1. (Color online) Distribution functions of errors from the minimax and Gauss–Legendre quadratures for $k=5$.

is above a threshold, go back to step (2) until convergence is achieved.

The standard Newton–Raphson scheme is used for the nonlinear optimizations in the above steps.

III. RESULTS AND DISCUSSION

The performance of the minimax approximation is investigated by comparing with other numerical quadratures. The integral (1.1) in $[0, \infty)$ can be estimated by the Gauss–Laguerre quadrature. It is, however, more accurate for the present purpose to use the Gauss–Legendre quadrature by changing the variable $s = t/(1-t)$. We compare the error distributions from the minimax and Gauss–Legendre quadratures for $k=5$ in Fig. 1. The minimax parameters are optimized at $R=100$. The error of the minimax approximation is distributed equally small in the range $x \in [1,100]$ in accord with the alternation theorem (2.9). The Gauss–Legendre quadrature is not accurate at both ends of the range.

For the application of the quadrature in the Laplace-transformed MP2 method, the interval of the MP2 energy denominator is

$$\Delta_{abij} \equiv \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j \in [E_{\min}, E_{\max}], \tag{3.1}$$

$$E_{\min} = 2(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}), \tag{3.2}$$

$$E_{\max} = 2(\varepsilon_{\max} - \varepsilon_{\min}), \tag{3.3}$$

where $\varepsilon_{\max}$ and $\varepsilon_{\min}$ are the maximum and minimum orbital energies, respectively, in the correlated calculation. The parameters in the minimax approximation $\{\omega_\nu^*\}$ and $\{\alpha_\nu^*\}$ are determined for $R = E_{\max}/E_{\min}$. Laplace-transformed MP2 energies are calculated using the scaled parameters $\{\bar{\omega}_\nu^* = \omega_\nu^*/E_{\min}\}$ and $\{\bar{\alpha}_\nu^* = \alpha_\nu^*/E_{\min}\}$. All of the quadrature methods are implemented in the GELLAN quantum chemistry program.[15]

Figures 2 and 3 show the absolute errors of the valence-shell and all-electron correlated Laplace-transformed MP2 energies for benzene using aug-cc-pVTZ and aug-cc-pCVTZ basis sets,[16–18] respectively. We used the geometrical parameters, $r_{CC} = 1.399$ Å and $r_{CH} = 1.087$ Å. In the valence-shell correlated case, the minimax approximation is more accurate
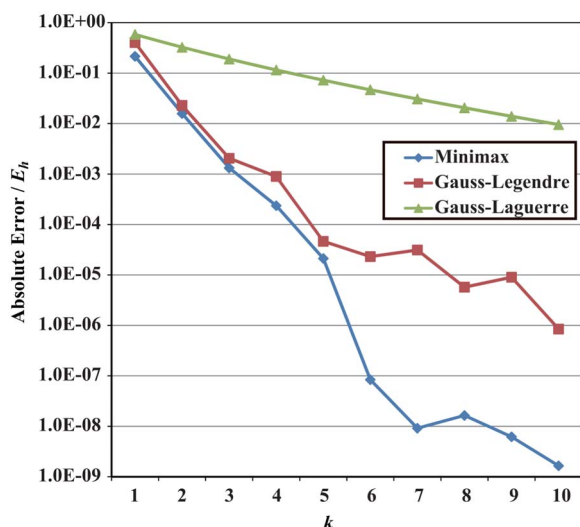
FIG. 2. (Color online) Absolute errors of the valence-shell Laplace-transformed MP2 energies for benzene with the aug-cc-pVTZ basis set. The supremum for the optimization is $R=56.06$.

FIG. 4. (Color online) Absolute errors of the valence-shell Laplace-transformed MP2 energies for ozone using the aug-cc-pVXZ basis sets (X =D, T, and Q).

than the Gauss–Legendre quadrature, especially for $k>5$. The error of the minimax quadrature energy decreases almost exponentially with respect to the number of quadrature points k in accord with the exponential decay of the Chebyshev norm.[14] The Gauss–Laguerre quadrature is much less accurate and is not suitable for Laplace MP2. More accurate quadratures are needed in the all-electron correlated case. Although the increased range $R=277.97$ worsens the convergences, the minimax quadrature is still accurate. The result of the Gauss–Legendre quadrature at $k=15$ is slightly less accurate than 1 mE_h, which is comparable with the minimax result at around $k=5$. Häser and Almlöf reported that the numerical quadrature scheme explicitly dependent on the energy denominators requires from eight to nine terms to obtain μE_h accuracy in the valence-shell correlated case.[3] The present result indicates that the minimax approximation is

comparable or even more accurate than the Häser–Almlöf scheme without treating the computationally unfavorable quartic energy denominators.

In Figs. 4 and 5, we compare the basis set dependencies of absolute errors for ozone with the geometrical parameters, $r_{OO}=1.266$ Å and $\angle_{OOO}=117.2°$, using the aug-cc-p(C)VXZ basis sets[16–18] with X=D, T, and Q. The maximum value R increases with the cardinal number of the basis, and the result becomes less accurate in general. The minimax approximation requires only $k=3$ for the results accurate to 1 mE_h in the valence-shell correlated case, while more than $k=5$ is needed to attain a similar accuracy in the all-electron correlated case. The present method is promising, especially when sufficient precision is required with a large R.

The computational cost for the minimax quadrature is negligibly small, e.g., an optimization with six iterations for
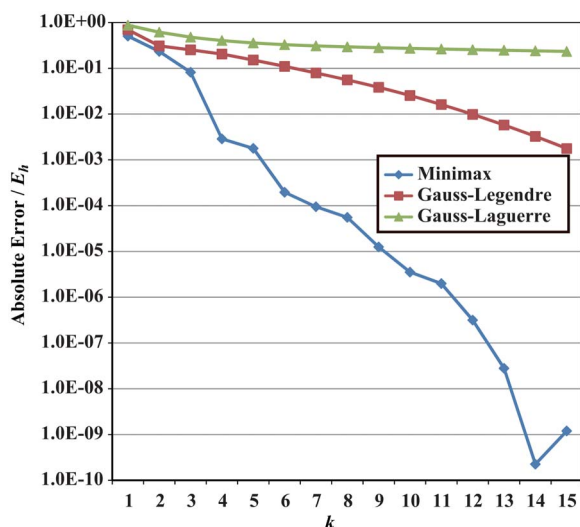

FIG. 3. (Color online) Absolute errors of the all-electron Laplace-transformed MP2 energies for benzene with the aug-cc-pCVTZ basis set. The supremum for the optimization is $R=277.97$.
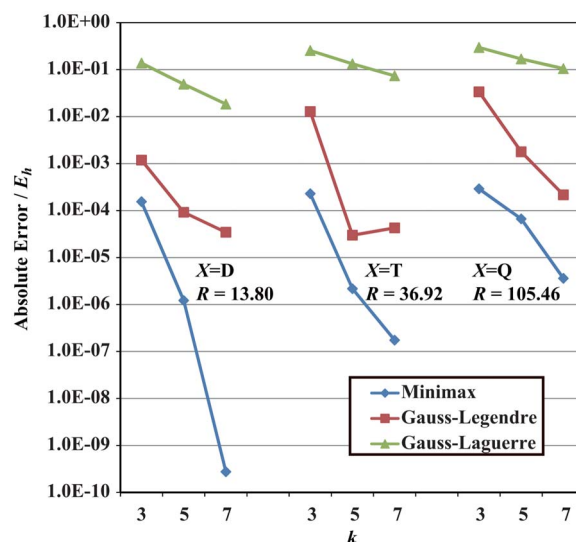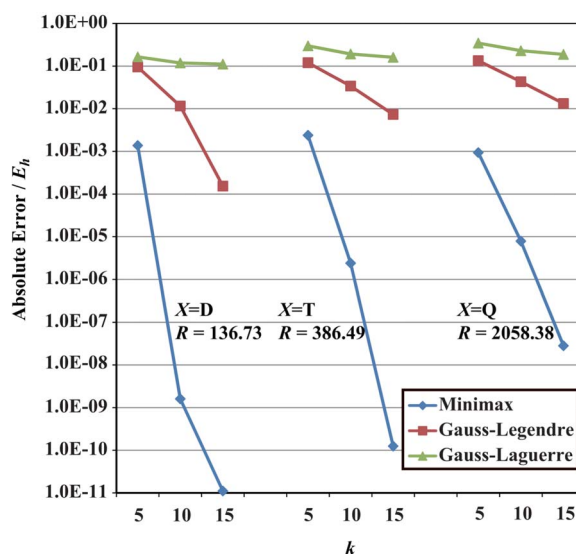

FIG. 5. (Color online) Absolute errors of the all-electron Laplace-transformed MP2 energy for ozone using the aug-cc-pVXZ basis sets (X =D, T, and Q).

$k=7$ takes less than 0.1 s. Although we have shown only the result for benzene and ozone, the convergence behaviors are similar for all of the other molecules we have examined. The minimax approximation is a useful tool due to its accuracy in the previous uses of the Laplace-transformed technique. It should be noted that the minimax quadrature in $[0, \infty)$ can also offer a useful approximation. For instance, the error of the quadrature in the all-valence MP2 energy of ozone with aug-cc-pVTZ is only 40 μE_h at $k=7$. In this case, the Remez optimization process can be skipped entirely.

Additionally, we describe another possible application of the technique in constructing hybrid quantum chemical methods. In the usual MP perturbation theories, a single Hamiltonian partitioning $\hat{H} = \hat{H}_0 + \hat{V}$ is used. However, a further splitting of the perturbation $\hat{V} = \hat{V}_A + \hat{V}_I$ leads to various hybrid approximations as possible combinations of the Hartree–Fock (HF), MP perturbation, and coupled-cluster (CC) methods, where $\hat{V}_A$ is the perturbation in a small active region embedded in the entire system. For instance, the amplitude equation of the CC-MP2 hybrid method is obtained by retaining the higher order contribution in $\hat{V}_A$ but only linear term in $\hat{V}_I$ as

$$\langle \mu | \exp(-\hat{T})(\hat{H}_0 + \hat{V}_A)\exp(\hat{T}) + \hat{V}_I | \mathrm{HF} \rangle = 0, \qquad (3.4)$$

such that the approximation is reduced to MP2 and CC in the limits of $\hat{V}_A = 0$ and $\hat{V}_A = \hat{V}$, respectively, for $E = \langle \mathrm{HF} | \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle$. Various choices of $\hat{V}_A$ exist, e.g., the use of a selection of (localized) molecular orbitals. One conceivable way is to employ orbitals nonorthogonal to the HF canonical orbitals,

$$\hat{V}_A = \frac{1}{4} \sum_{\pi\theta\rho\sigma} \langle \pi\theta \| \rho\sigma \rangle \{a_\pi^+ a_\theta^+ a_\sigma a_\rho\}, \qquad (3.5)$$

where $\pi, \theta, \ldots$, denote active orthonomalized orbitals spanned by AOs only with active atomic centers and the braces $\{\}$ denote normal ordering with respect to the Hartree–Fock vacuum.[19] The hybrid CC-MP2 method can be relatively easily implemented by a small modification of a CC program. It is evident that the treatment of only $\hat{V}_A$ in the CC iteration makes the application of CC to large molecules feasible, retaining the accuracy in the active part. Nevertheless, when we use a perturbational treatment such as the "golden standard" CCSD(T) method[20] in $\hat{V}_A$, it is more advantageous to drive objects in the active basis, $\pi, \theta, \ldots$, with much less dimension. This requires the decomposition of energy denominators for triple amplitudes,

$$\langle \mu_3 | [\hat{H}_0, \hat{T}_3] + (\hat{V}_A \hat{T}_2)_c | \mathrm{HF} \rangle = 0, \qquad (3.6)$$

without explicit treatment of $\hat{T}_3$ in the full dimension. The GELLAN program was originally initiated with the intention of the development of such hybrid methods.[15] We are going to examine the effectiveness of the Laplace-transformed technique with the minimax approximation for these purposes.

IV. SUMMARY

In this paper, we have introduced the minimax approximation in Laplace-transformed MP perturbation theories. The best approximation is defined by minimizing the Chebyshev norm of the error in the given interval. We have illustrated the optimization scheme based on the alternation theorem. The minimax approximation was applied to the Laplace-transformed MP2 calculation to exhibit fast convergences with respect to the number of quadrature points k. In the valence-shell correlated case, the number of quadrature points, $k=5$, is generally sufficient for MP2 energies accurate to a few 10 μE_h, while almost $k=10$ is needed for a similar accuracy in the all-electron correlated case. Although the convergence is somewhat slower in the latter case, the minimax approximation is significantly more accurate than the other numerical quadratures examined in this work.

The optimization code of the minimax quadrature in the Laplace-transformed technique is available upon request. In addition, various precalculated cases are presented in Ref. 21.

[1] S. Saebø and P. Pulay, Annu. Rev. Phys. Chem. **44**, 213 (1993).
[2] J. Almlöf, Chem. Phys. Lett. **176**, 319 (1991).
[3] M. Häser and J. Almlöf, J. Chem. Phys. **96**, 489 (1992).
[4] M. Häser, Theor. Chim. Acta **87**, 147 (1993).
[5] A. K. Wilson and J. Almlöf, Theor. Chim. Acta **95**, 49 (1997).
[6] P. Y. Ayala and G. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
[7] D. S. Lambrecht, B. Doser, and C. Ochsenfeld, J. Chem. Phys. **123**, 184102 (2005).
[8] S. Schweizer, B. Doser, and C. Ochsenfeld, J. Chem. Phys. **128**, 154101 (2008).
[9] Y. Jung, R. C. Lochan, A. D. Dutoi, and M. Head-Gordon, J. Chem. Phys. **121**, 9793 (2004).
[10] A. F. Izmaylov and G. E. Scuseria, Phys. Chem. Chem. Phys. **10**, 3421 (2008).
[11] P. R. Surján, Chem. Phys. Lett. **406**, 318 (2005).
[12] M. Kobayashi and H. Nakai, Chem. Phys. Lett. **420**, 250 (2006).
[13] D. Braess, *Nonlinear Approximation Theory* (Springer-Verlag, Berlin, 1986).
[14] D. Braess and W. Hackbusch, IMA J. Numer. Anal. **25**, 685 (2005).
[15] GELLAN, A hierarchical quantum chemistry program, Nagoya University.
[16] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[17] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6769 (1992).
[18] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **103**, 4572 (1995).
[19] See, for instance, I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986).
[20] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[21] See http://www.mis.mpg.de/scicomp/EXP_SUM/1_x/tabelle for more optimization codes of the minimax quadrature in the Laplace-transformed technique.