Communication: A new approach to dual-basis second-order Møller–Plesset calculations

Jia Deng and Peter M. W. Gill[a)]
Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

We describe a hierarchy of approximations (MP2[x]) that allow one to estimate second-order Møller–Plesset (MP2) energies in a large basis set from small-basis calculations. The most cost-effective approximation, MP2[K], is significantly cheaper than full MP2 but numerical tests on small atoms and molecules indicate that it is nonetheless accurate. We conclude that MP2[K] is an attractive level of theory for large systems. © *2011 American Institute of Physics*. [doi:10.1063/1.3556705]

I. INTRODUCTION

Accurate prediction of molecular properties from first principles[1] requires quantum mechanical methods that incorporate electron correlation, *i.e.*, effects beyond the Hartree–Fock (HF) model. Second-order Møller–Plesset perturbation theory[2] (MP2) offers one of the most cost-effective methods to include these and, although it is less economical than density functional approaches, it enjoys the advantage of naturally and properly accounting for medium- and long-range correlation.[3] Nonetheless, its $O(N^5)$ cost has been a significant obstacle to its application in large systems.

There has, however, been significant progress toward reducing this cost. Methods such as local MP2 (LMP2),[4,5] cutoff-based Laplace-transform MP2,[6–8] atomic-orbital-based (AO)-based LMP2,[9] and scaled-opposite-spin MP2 (Ref. 10) have costs that grow more slowly with N and have extended the scope of MP2 to much larger systems. Other developments, based on the resolution of the identity (RI) (Refs. 11 and 12) or the pseudospectral method,[13] do not alter the fifth-order scaling but have dramatically reduced prefactors. Finally, we note the extraordinary speeds that can be achieved[14,15] in MP2 calculations by exploiting graphics processing units, rather than central processing units.

We are interested in pursuing large basis set MP2 calculations on chemically interesting systems, but such systems often possess compact three-dimensional structures, and the savings achieved by local methods can sometimes be disappointing. Moreover, the neglect of contributions from distant electron pairs can lead to the underestimation of physically significant dispersion interactions. It is clearly desirable to develop alternative methods that improve computational speed while maintaining accuracy.

It is well known that, although the cost of a small-basis (primary) HF calculation is significantly less than that of a large-basis (secondary) calculation, the occupied primary molecular orbitals (MOs) are often similar to the secondary ones. This led us recently to develop perturbative approaches that "bootstrap" from small-basis HF calculations toward large-basis HF energies[16–18] and, in the present work, we extend these ideas, investigating a hierarchy of approximations that estimate large-basis MP2 energies using cheap small-basis MOs.

Unlike earlier dual-basis MP2 (DB-MP2) methods,[19–21] which use *approximate* secondary MOs and an *approximate* secondary HF energy, our methods employ the *exact* MOs and energy. Notwithstanding this, our methods achieve savings in the bottleneck step (the first quarter transformation of the two-electron integrals) and are, thus, well suited for MP2 calculations with large basis sets.

II. THEORY

In a closed-shell system of $2O$ electrons, a self-consistent field (SCF) calculation[22,23] in a (secondary) basis set of N functions yields O occupied and $N - O$ virtual MOs. These orbitals and their associated energies yield the (secondary) MP2 correlation energy[24]

$$E^{(2)} = \sum_{ij}^{occ} \sum_{ab}^{virt} \frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \tag{1}$$

The electron repulsion integrals (ERIs) in the MO basis are formed from the AO integrals via the integral transformation[24]

$$(ia|jb) = \sum_{\mu\nu\lambda\sigma}^{N} C_\mu^i C_\nu^a C_\lambda^j C_\sigma^b (\mu\nu|\lambda\sigma) \tag{2}$$

and, for maximum efficiency, this is performed in four quarter transformations. The first of these, which is normally the most expensive, requires ON^4 multiply-adds.

Our dual-basis MP2 reduces this computational bottleneck by avoiding the full integral transformation in the secondary basis. We begin with a full secondary HF calculation, to obtain the secondary HF energy, MOs, and orbital energies. However, instead of then constructing the exact secondary ERIs using Eq. (2), we perform a cheaper HF calculation in a primary basis of $n \ll N$ functions, to obtain O occupied orbitals and $n - O$ virtuals (Fig. 1). We then use the maximum overlap method[25] to divide the secondary virtuals into those that correspond to the primary virtuals (*viz.*, the S_2 space) and those that comprise the extended virtual space S_3.

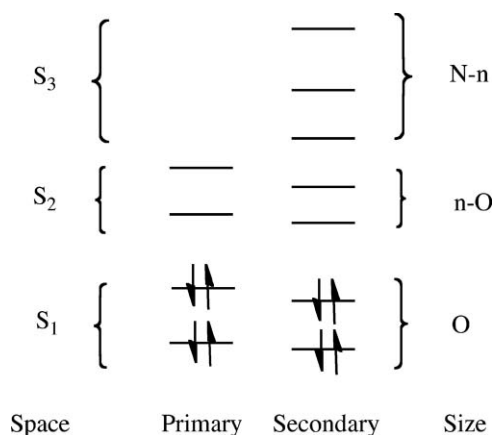a)Electronic mail: peter.gill@anu.edu.au.

FIG. 1. Orbital spaces in the dual-basis framework

We then write each secondary ERI as the sum

$$(i_S a_S | j_S b_S) = (i_P a_P | j_P b_P)$$

$$+ \Delta_i + \Delta_a + \Delta_j + \Delta_b \tag{3a}$$

$$+ \Delta_{ib} + \Delta_{aj} + \Delta_{ab} \tag{3b}$$

$$+ \Delta_{ia} + \Delta_{jb} \tag{3c}$$

$$+ \Delta_{ij} \tag{3d}$$

$$+ \Delta_{iaj} + \Delta_{iab} + \Delta_{ijb} + \Delta_{ajb} \tag{3e}$$

$$+ \Delta_{iajb} \tag{3f}$$

of the corresponding primary ERI $(i_P a_P | j_P b_P)$, the one-orbital corrections [Eq. (3a)], two-orbital corrections [Eqs. (3b)–(3d)], three-orbital corrections [Eq. (3e)], and four-orbital corrections [Eq. (3f)]. These corrections are ERIs over primary and difference orbitals

$$i_\delta = \begin{cases} i_S & i \in S_3 \\ i_S - i_P & i \notin S_3 \end{cases} \tag{4}$$

and, thus, for example,

$$\Delta_i = (i_\delta a_P | j_P b_P) = (i_S a_P | j_P b_P) - (i_P a_P | j_P b_P). \tag{5}$$

The primary ERIs are cheap to form, the one-orbital corrections are more expensive, the two-electron corrections are even more expensive, and so on. These costs are summarized in Table I and suggest a hierarchy of progressively more accurate, but expensive, approximations to the secondary ERIs. Accordingly, we define the MP2[1], MP2[K], MP2[J], MP2[2], and MP2[3] integrals as resulting from truncation after Eqs. (3a), (3b), (3c), (3d) or (3e), respectively. The MP2[4] integrals, of course, are exactly the secondary integrals $(ia|jb)$ (we note that the cost of the subtractions in equations such as Eq. (5) grows only quartically with n and N).

We note for MP2[1] and MP2[K] the cost of the subsequent transformation with $O^2 N^3$ scaling is also reduced by N^2/n and N/n compared to conventional MP2. This reduction is important if the AO integrals are sparse.

TABLE I. Costs (multiply-adds) of the first quarter integral transformation in the MP2[x] approximations (n = size of primary basis set; N = size of secondary basis set; O = number of occupied orbitals; P represents a primary MO; S represents a secondary MO).

	Required integrals	Cost of quarter transformation	Cost ratio
MP2[0]	(PP|PP)	$O n^4$	$(N/n)^4$
MP2[1]	+ (SP|PP)	+ $O n^3 N$	$(N/n)^3$
MP2[K]	+ (PS|PS)	+ $O n^2 N^2$	$(N/n)^2$
MP2[J]	+ (SS|PP)	+ $O n^2 N^2$	$\frac{1}{2}(N/n)^2$
MP2[2]	+ (PS|PS)	+ $O n^2 N^2$	$\frac{1}{3}(N/n)^2$
MP2[3]	+ (SS|SP)	+ $O n N^3$	(N/n)
MP2	+ (SS|SS)	+ $O N^4$	1

The MP2[x] total energy, which we will denote by

MP2[x]/(primary basis)/(secondary basis)

is then the sum of the exact secondary HF energy and the correlation energy (1) using the MP2[x] integrals. We eschew the possibility of using an approximate dual-basis secondary HF energy because the HF component is not rate-limiting in MP2 calculations on large systems. For convenience, we define the MP2[0] as the normal MP2 energy in the primary basis.

III. RESULTS

A. H₂ molecule

To provide interested readers with benchmark results for their own code development, we calculated the MP2[x]/primary/cc-pV5Z energy of H_2 ($R = 1.4$ bohr), using a sequence of increasingly accurate primary bases. Table II reveals that the MP2/primary errors range from 38 to 0.7 mE_h, but that there are dramatic improvements at the MP2[K] and MP2[3] levels (2–3 and 3–5 orders of magnitude, respectively). We are particularly encouraged by the accuracy achieved with STO-3G primary basis because it contains only one s function per H atom. The MP2/STO-3G energy lies 38 mE_h above the MP2/cc-pV5Z energy but this crude starting point yields a MP2[K]/STO-3G/cc-pV5Z energy that misses MP2/cc-pV5Z by only 1 mE_h, which is almost as good as MP2/cc-pVQZ. Moreover, we see that MP2[K] with primary bases beyond cc-pVDZ incurs negligible errors.

TABLE II. Deviation (hartree) of MP2[x]/primary/cc-pV5Z energies from MP2/cc-pV5Z for the H_2 molecule.

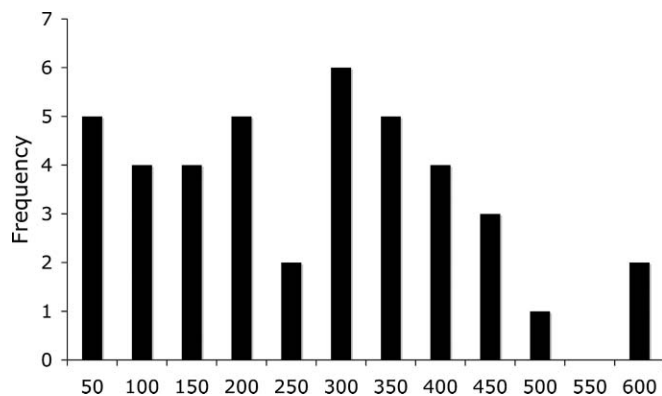|	STO-3G	cc-pVDZ	cc-pVTZ	cc-pVQZ
N/n	70	14	5	2
MP2[0]	3.8×10^{-2}	1.2×10^{-2}	2.6×10^{-3}	7.1×10^{-4}
MP2[1]	1.5×10^{-2}	-2.1×10^{-3}	-3.2×10^{-3}	1.6×10^{-4}
MP2[K]	-9.6×10^{-4}	1.8×10^{-4}	-2.6×10^{-6}	-2.1×10^{-7}
MP2[J]	-6.4×10^{-4}	1.2×10^{-4}	4.1×10^{-6}	3.7×10^{-7}
MP2[2]	-6.5×10^{-4}	1.2×10^{-4}	3.9×10^{-6}	3.6×10^{-7}
MP2[3]	7.7×10^{-5}	7.9×10^{-6}	9.5×10^{-8}	5.2×10^{-9}

FIG. 2. Absolute errors (kJ/mol) of MP2[0]/cc-pVDZ/cc-pVTZ for our test set.
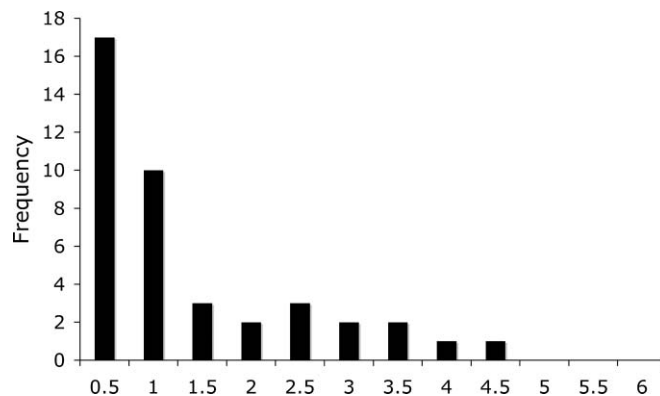

FIG. 3. Absolute errors (kJ/mol) of MP2[K]/cc-pVDZ/cc-pVTZ for our test set.

B. Computational details

In our work on HF perturbative corrections,[16,17] we found that cc-pVDZ is an effective primary basis when the secondary basis is cc-pVTZ. To study the MP2[x] approximations, we, therefore, computed MP2[x]/cc-pVDZ/cc-pVTZ energies for the first-row atoms (He–Ne) and the 32 neutral molecules based on these atoms in the G1 data set.[26] To facilitate comparisons with the DB-MP2 method, we have also performed MP2[x]/rcc-pVTZ/cc-pVTZ calculations on the same test set of 41 systems. All geometries were optimized at the B3LYP/6-31G($2df$, p) level. Calculations on open-shell systems used the unrestricted Hartree–Fock formalism. SCF convergence required a direct inversion in the iterative space (DIIS) error of 10^{-7} using integral cutoffs of 10^{-14}. Cartesian d and f functions were used.

C. Accuracy of MP2[x]

Table III summarizes the MP2[x] deviations from exact MP2 energies, giving the mean signed error (MSE), mean absolute error (MAE), maximum error (Max), and number of outliers (NO) (≥ 4 kJ/mol). The raw data are available in the supplementary material.[27]

The MP2[0] $\equiv$ MP2/cc-pVDZ energies underestimate the MP2/cc-pVTZ values by 237 kJ/mol on average and Fig. 2 shows the distribution of these errors. Given such large differences, one may wonder how effective the one-orbital corrections [Eq. (3a)] will be and it is, therefore, encouraging to find that the MP2[1] energies (MAE = 26 kJ/mol) are generally much more accurate than the MP2[0] ones. However, inspection of the individual errors reveals that the im-

TABLE III. Errors (kJ/mol) of MP2[x]/cc-pVDZ/cc-pVTZ, relative to MP2/cc-pVTZ, for our test set

	MAE	MSE	Max	NO
MP2[0]	236.9	236.9	574.5	41
MP2[1]	25.7	11.4	82.1	41
MP2[K]	1.10	0.92	4.1	1
MP2[J]	0.32	0.21	1.1	0
MP2[2]	0.30	0.17	1.0	0
MP2[3]	0.07	0.03	0.4	0

provement is not uniform and, for example, whereas the error drops by more than an order of magnitude for H_2O_2, the improvement is less than a factor of 2 for Li. This would seem to preclude the development of a useful "scaling factor" scheme.

The MP2[K] energies are striking and the extraordinary improvement between MP2[1] and MP2[K] reveals the importance of pair-correlation between orbitals in the extended space S_3. As Fig. 3 shows, the MP2[K] errors are consistently 2 orders of magnitude smaller than the MP2[0] errors. On average, their deviations from the exact MP2 energies are only 1 kJ/mol and even the largest discrepancy (CO_2) is only 4 kJ/mol. Such discrepancies will be tolerable in many chemical applications.

MP2[J] is significantly more accurate than MP2[K] but incurs twice the cost. MP2[2] is yet more expensive but is almost identical to MP2[J], indicating that the relaxation of occupied orbitals upon basis set extension is negligible.

MP2[3] energies are almost indistinguishable (MAE = 0.07 kJ/mol) from the exact MP2 values. However, although it is reassuring to see that the MP2[x] hierarchy converges smoothly toward exact MP2, the cost of MP2[3] is much greater than MP2[2] and we, therefore, doubt that MP2[3] will have much practical utility.

D. Comparison with DB-MP2

Recent work[21,28] has shown that the DB-MP2 method (*i.e.*, applying MP2 theory to the approximate orbitals from a dual-basis HF calculation) is more accurate than the Wolinski–Pulay scheme,[20] and it is, therefore, interesting to compare it with MP2[x]. To this end, we have used both methods with the rcc-pVTZ primary basis[29] to target the MP2/cc-pVTZ energies of our test set.

Table IV shows that DB-MP2 and MP2[K] are broadly comparable, with MAEs of 0.6 and 0.3 kJ/mol, respectively. A detailed analysis reveals that the slight superiority of MP2[K] stems from its use of the exact secondary HF energy.

Because our pilot MP2[x] implementation is unoptimized, we have not yet attempted timing comparisons with DB-MP2. However, comparisons can still be made based on theoretical arguments.

TABLE IV. Errors (kJ/mol) of MP2[x]/rcc-pVTZ/cc-pVTZ and DB-MP2/rcc-pVTZ/cc-pVTZ, relative to MP2/cc-pVTZ, for our test set.

	MAE	MSE	Max	NO
MP2[0]	72.1	72.1	160.1	39
MP2[1]	21.7	−8.8	131.8	32
DB-MP2	0.55	0.55	2.6	0
MP2[K]	0.32	0.27	1.1	0
MP2[J]	0.07	0.06	0.3	0
MP2[2]	0.06	0.05	0.3	0
MP2[3]	0.02	0.0	0.2	0

DB-MP2 employs the efficient DB–HF algorithm for the fourth-order secondary HF reference calculation, but leaves the fifth-order MP2 component untouched. As a result, DB-MP2 is very effective for small- to medium-sized systems, where the underlying HF calculation is the bottleneck. For larger systems, DB-MP2 becomes less efficacious but the MP2[x] approximations become increasingly competitive. For example, as Table I shows, MP2[K] and MP2[J] are cheaper than MP2 by factors of $N^2/(n^2)$ and $N^2/(2n^2)$, respectively. To illustrate these, the cc-pVTZ/cc-pVDZ ratio for our test set is roughly 2.5, which implies speedup factors of 6 and 3, respectively.

Steele *et al.*[21] have shown that the usefulness of DB-MP2 is enhanced when it is combined with the RI approximation. In the same way, it is not difficult to develop RI versions of the MP2[x] approximations and these will yield even greater computational savings.

IV. CONCLUDING REMARKS

We have examined a hierarchy of schemes that use the results of a small-basis HF calculation to approximate a large-basis MP2 energy. Our methods reduce the cost of the integral transformation steps and are, therefore, well suited for MP2 calculations on large systems.

We have tested the accuracy of our methods using the cc-pVDZ/cc-pVTZ basis set pair on a set of 41 atoms and molecules. The MP2[K] and MP2[J] energies are close to true MP2 energies (MAEs of 1.1 and 0.3 kJ/mol, respectively) but will be considerably faster. MP2[3] is even more accurate, but may not be much faster than full MP2. We anticipate that MP2[K] is probably the best compromise between cost and accuracy.

The MP2[x] hierarchy can be incorporated into existing MP2 software and we will report timing results from the Q-CHEM package[30] in a forthcoming paper.

ACKNOWLEDGMENTS

[1] W. J. Hehre, L. Radom, P. v.R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
[2] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[3] S. Grimme, J. Chem. Phys. **124**, 034108 (2006).
[4] S. Saebo and P. Pulay, Annu. Rev. Phys. Chem. **44**, 213 (1993).
[5] M. Schutz, G. Hetzer, and H. J. Werner, J. Chem. Phys. **111**, 5691 (1999).
[6] P. Ayala and G. E. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
[7] P. Ayala, K. Kudin, and G. E. Scuseria, J. Chem. Phys. **115**, 9698 (2001).
[8] B. Doser, D. Lambrecht, J. Kussmann, and C. Ochsenfeld, J. Chem. Phys. **130**, 064107 (2009).
[9] M. S. Lee, P. E. Maslen, and M. Head-Gordon, J. Chem. Phys. **112**, 3592 (2000).
[10] Y. Jung, R. C. Lochan, A. D. Dutoi, and M. Head-Gordon, J. Chem. Phys. **121**, 9793 (2004).
[11] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, Chem. Phys. Lett. **294**, 143 (1998).
[12] M. Feyereisen, G. Fitzgerald, and A. Komornicki, Chem. Phys. Lett. **208**, 359 (1993).
[13] R. A. Friesner, R. B. Murphy, M. D. Beachy, M. N. Ringnalda, W. T. Pollard, B. D. Dunietz, and Y. Cao, J. Phys. Chem. A **103**, 1913 (1999).
[14] R. Olivares-Amaya, M. A. Watson, R. G. Edgar, L. Vogt, Y. Shao, and A. Aspuru-Guzik, J. Chem. Theory Comput. **6**, 135 (2010).
[15] M. A. Watson, R. Olivares-Amaya, R. G. Edgar, and A. Aspuru-Guzik, Comput. Sci. Eng. **12**(4), 40 (2010).
[16] J. Deng, A. T. B. Gilbert, and P. M. W. Gill, J. Chem. Phys. **130**, 231101 (2009).
[17] J. Deng, A. T. B. Gilbert, and P. M. W. Gill, J. Chem. Phys. **133**, 044116 (2010).
[18] J. Deng, A. T. B. Gilbert, and P. M. W. Gill, Phys. Chem. Chem. Phys. **12**, 10759 (2010).
[19] R. Jurgens-Lutovsky and J. Almlöf, Chem. Phys. Lett. **178**, 451 (1991).
[20] K. Wolinski and P. Pulay, J. Chem. Phys. **118**, 9497 (2003).
[21] R. P. Steele, R. A. DiStasio, Jr., Y. Shao, J. Kong, and M. Head-Gordon, J. Chem. Phys. **125**, 074108 (2006).
[22] G. G. Hall, Proc. R. Soc. London, Ser. A **205**, 541 (1951).
[23] C. C.J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
[24] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989).
[25] A. T. B. Gilbert, N. A. Besley, and P. M. W. Gill, J. Phys. Chem. A **112**, 13164 (2008).
[26] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989).
[27] See supplementary material at http://dx.doi.org/10.1063/1.3556705 for raw MP2[x] energies.
[28] M. S. Marshall, J. S. Sears, L. A. Burns, J.-L. Bredas, and C. D. Sherrill, J. Chem. Theory Comput. **6**, 3681 (2010).
[29] We chose this primary basis because the DB-RI-MP2 method stipulates that the primary basis be a subset of the secondary basis. There is no such restriction in the MP2[x] approximations.
[30] Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio, Jr., R. C. Lochan, T. Wang, G. J.O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. V. Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F.C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C. P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Z. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. WoodcockIII, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon, Phys. Chem. Chem. Phys. **8**, 3172 (2006).