Stochastic Formulation of the Resolution of Identity: Application to Second Order Møller–Plesset Perturbation Theory

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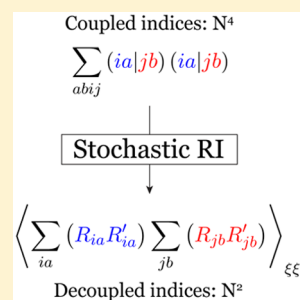
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ABSTRACT: A stochastic orbital approach to the resolution of identity (RI) approximation for 4-index electron repulsion integrals (ERIs) is presented. The stochastic RI-ERIs are then applied to second order Møller–Plesset perturbation theory (MP2) utilizing a *multiple stochastic orbital approach*. The introduction of multiple stochastic orbitals results in an $O(N_{AO}^3)$ scaling for both the stochastic RI-ERIs and stochastic RI-MP2, N_{AO} being the number of basis functions. For a range of water clusters we demonstrate that this method exhibits a small prefactor and observed scalings of $O(N_e^{2.4})$ for total energies and $O(N_e^{3.1})$ for forces (N_e being the number of correlated electrons), outperforming MP2 for clusters with as few as 21 water molecules.

Coupled indices: N^4

$$\sum_{abij} (ia|jb)(ia|jb)$$

Stochastic RI

$$\left\langle \sum_{ia} (R_{ia}R_{ia}') \sum_{jb} (R_{jb}R_{jb}') \right\rangle_{\xi\xi'}$$

Decoupled indices: N^2

INTRODUCTION

The vast majority of *ab initio* electronic structure methods require the calculation of 4-index electron repulsion integrals (ERIs). In fact, in some instances, when atom-centered Gaussian basis sets are used, the calculation of these integrals and their transformation from the atomic orbital (AO) to the molecular orbital (MO) basis are the computational bottleneck, *e.g.*, second order Møller–Plesset perturbation theory (MP2). An appreciable reduction in the computational prefactor may be obtained through the resolution of identity (RI) approximation, also known as the density fitting approximation.[1−5] The RI approximation expresses the 4-index ERIs in terms of 2-index and 3-index ERIs, the former being evaluated in an auxiliary basis and the latter as a combination of the AO and auxiliary basis sets. Since only 2- and 3-index ERIs are needed, the RI approximation reduces the total number of integrals to be calculated and transformed. Today it has become common practice to apply the RI approximation to 4-index ERIs in order to lower the computational prefactor. However, in spite of these benefits, the assembly of the approximate ERIs scales as $O(N^5)$, N being the number of basis functions, and therefore the scaling remains unaltered. Recent work focused on mitigating the high computational cost associated with the 4-index ERIs, through the application of a tensor decomposition technique known as tensor hypercontraction,[6−8] has resulted in flexible factorization of the ERIs and reduced scaling.

As an alternative to reduced scaling techniques focused on the ERIs, stochastic approaches to performing traditional electronic structure calculations have proven effective in reducing the high computational cost.[9−27] There are many successful stochastic techniques that can handle increasingly larger systems. We note, for example, that in certain situations the full configuration-interaction quantum Monte Carlo approach can handle systems with tens of electrons.[9−12] Likewise, auxiliary-field Monte Carlo which replaces the two-body interaction by an interaction with fluctuating densities and the fixed-node approximation,[28] when combined with the shifted-contour approach[29] give excellent results for systems with tens of electrons.[30] For large systems containing hundreds or thousands of electrons several of the authors have developed stochastic methods for DFT and TDDFT,[21,26,27,31] MP2,[19,24] GF2,[32] GW,[25,33−35] and the Bethe-Salpeter equation.[25]

Given the success of the RI approximation and stochastic electronic structure methods, it is therefore conceivable that methods that bring together the strengths of both approaches could prove extremely beneficial. In this letter, we present a hybrid approach, stochastic resolution of identity (sRI), that (i) lowers the computational scaling of the RI approximation to the 4-index ERIs and (ii) decouples pairs of indices within the 4-index ERI expression, a general feature capable of bringing about additional method-specific reductions in scaling. We apply the sRI approximation to the time-integrated MP2 expression and obtain an observed scaling of $O(N_e^{2.4})$, where N_e is the number of correlated electrons.

THEORY

We use the usual notation, where the occupied, virtual, and general sets of MOs are represented by the indices $i, j, k, ...; a, b, c, ...;$ and $p, q, r, ...,$ respectively. The AO Gaussian basis functions are represented by $\chi_\alpha(r)$ and Greek indices $\alpha, \beta, \gamma, \delta, ...,$ while the auxiliary basis functions are represented by the indices $A, B, ...$ Finally, the total number of AO basis functions, auxiliary basis functions, occupied MOs, and virtual MOs are $N_{AO}, N_{aux}, N_{occ},$ and $N_{virt},$ respectively. Further, both N_{aux} and N_{AO} are proportional to the system size with $N_{aux},$ typically 3−6 times $N_{AO}.$

Deterministic Resolution of Identity. The 4-, 3-, and 2-index ERIs are defined as

$$(\alpha\beta|\gamma\delta) = \iint dr_1 \, dr_2 \, \frac{\chi_\alpha(r_1)\,\chi_\beta(r_1)\,\chi_\gamma(r_2)\,\chi_\delta(r_2)}{r_{12}}$$

$$(\alpha\beta|A) = \iint dr_1 \, dr_2 \, \frac{\chi_\alpha(r_1)\,\chi_\beta(r_1)\,\chi_A(r_2)}{r_{12}} \tag{1}$$

$$V_{AB} = \iint dr_1 \, dr_2 \, \frac{\chi_A(r_1)\,\chi_B(r_2)}{r_{12}}$$

The approximate 4-index RI-ERIs are then expressed symmetrically in terms of the lower-rank integrals according to

$$(\alpha\beta|\gamma\delta) \approx \sum_{AB}^{N_{aux}} (\alpha\beta|A)[V^{-1}]_{AB}(B|\gamma\delta)$$

$$= \sum_{Q}^{N_{aux}} \Big[\sum_{A}^{N_{aux}} (\alpha\beta|A)[V^{-1/2}]_{AQ} \Big] \Big[\sum_{B}^{N_{aux}} [V^{-1/2}]_{QB} (B|\gamma\delta) \Big] \tag{2}$$

Defining

$$K_{\alpha\beta}^{Q} \equiv \sum_{A}^{N_{aux}} (\alpha\beta|A)V_{AQ}^{-1/2} \tag{3}$$

yields

$$(\alpha\beta|\gamma\delta) \approx \sum_{Q}^{N_{aux}} K_{\alpha\beta}^{Q} K_{\gamma\delta}^{Q} \tag{4}$$

Summations over A and B (eqs 2 and 3) are usually performed beforehand, and their contractions, $K_{\alpha\beta}^{Q}$ and $K_{\gamma\delta}^{Q}$, scale as $O(N_{AO}^2 N_{aux})$ while the construction of $V^{-1/2}$ scales as $O(N_{aux}^3)$. By expressing eq 2 in terms of $K_{\alpha\beta}^{Q}$ and $K_{\gamma\delta}^{Q}$ (eq 4), the approximate ERIs now scale as $O(N_{AO}^4 N_{aux})$.

ERIs are most often used in the MO basis, and their transformation from the AO basis is done is done in a two-step process with both the first and the second transformations (eq 5) costing $O(N_{AO}^3 N_{aux})$.

$$K_{p\gamma}^{Q} = \sum_{\alpha}^{N_{AO}} C_{\alpha}^{p} K_{\alpha\gamma}^{Q}$$

$$K_{pq}^{Q} = \sum_{\gamma}^{N_{AO}} C_{\gamma}^{q} K_{p\gamma}^{Q} \tag{5}$$

According to eq 4 the cost of computing the RI-ERIs scales as $O(N_{AO}^4 N_{aux})$; however, the total number of integrals that must be calculated grows only as $O(N_{AO}^2 N_{aux})$. Since both N_{AO} and N_{aux} are dependent on the system size, the principle advantage of the RI approximation is its ability to reduce the total number of integrals that must be calculated and stored while maintaining the same overall scaling.

Stochastic Resolution of Identity. The stochastic RI approximation we develop here utilizes the same set of 2- and 3-index ERIs while introducing an additional set of N_s stochastic orbitals, $\{\theta^\xi\}, \xi = 1, 2, ..., N_s.$ The stochastic orbitals are defined as arrays of length N_{aux} with randomly selected elements $\theta_A^\xi = \pm 1.$ The stochastic orbitals have the following property:

$$\langle \theta \otimes \theta^T \rangle_\xi = I \tag{6}$$

where we have denoted the stochastic average over N_s stochastic orbitals by $\langle ... \rangle_\xi$. To better illustrate this, consider the case where the set $\{\theta^\xi\}$ contains N_s elements, where each array θ^ξ is of length $N_{aux} = 2$. The resulting stochastic average is then

$$\langle \theta \otimes \theta^T \rangle_\xi = \frac{1}{N_s} \sum_{\xi=1}^{N_s} \theta^\xi \otimes (\theta^\xi)^T \equiv \begin{pmatrix} \langle \theta_1\theta_1 \rangle_\xi & \langle \theta_1\theta_2 \rangle_\xi \\ \langle \theta_2\theta_1 \rangle_\xi & \langle \theta_2\theta_2 \rangle_\xi \end{pmatrix} \tag{7}$$

The individual matrix elements may be grouped as diagonal and off-diagonal elements. The stochastic average of the diagonal elements, $\langle \theta_A\theta_A \rangle_\xi$, is 1, and the stochastic average of the off-diagonal elements, $\langle \theta_A\theta_B \rangle_\xi$, converges to 0 as $N_s \to \infty$, due to the random oscillations of $\theta_A^\xi \theta_B^\xi$ between ± 1. The above example shows that the introduction of an identity matrix can be recast as the stochastic average over outer products of stochastic orbitals and is the underlying principle of the stochastic resolution of identity method.

The deterministic RI-ERIs in eq 2 are expressed symmetrically in terms of the 2-index and 3-index ERI matrix elements with the symmetric parts being coupled through a summation over the index Q. Inserting the stochastic identity matrix, we obtain the expression for the sRI-ERIs:

$$(\alpha\beta|\gamma\delta) \approx \sum_{PQ}^{N_{aux}} \sum_{AB}^{N_{aux}} (\alpha\beta|A)V_{AP}^{-1/2} I_{PQ} V_{QB}^{-1/2} (B|\gamma\delta)$$

$$= \sum_{PQ}^{N_{aux}} \sum_{AB}^{N_{aux}} (\alpha\beta|A)V_{AP}^{-1/2} (\langle \theta \otimes \theta^T \rangle_\xi)_{PQ} V_{QB}^{-1/2} (B|\gamma\delta)$$

$$= \Big\langle \Big[\sum_{A}^{N_{aux}} (\alpha\beta|A) \sum_{P}^{N_{aux}} V_{AP}^{-1/2} \theta_P \Big] \Big[\sum_{B}^{N_{aux}} (B|\gamma\delta) \sum_{Q}^{N_{aux}} \theta_Q^T V_{QB}^{-1/2} \Big] \Big\rangle_\xi \tag{8}$$

where $(\langle \theta \otimes \theta^T \rangle_\xi)_{PQ}$ is the PQth element of the stochastic identity matrix. We now define the ξth elements of the stochastic average as

$$R_{\alpha\beta}^{\xi} = \sum_{A}^{N_{aux}} (\alpha\beta|A) \Big[\sum_{P}^{N_{aux}} [V_{AP}^{-1/2} \theta_P^\xi] \Big] \equiv \sum_{A}^{N_{aux}} (\alpha\beta|A) L_A^{\xi} \tag{9}$$

With this definition, the ERI in the AO basis (eq 8) is now given by a stochastic average, an $O(N_s N_{AO}^4)$ step:

$$(\alpha\beta|\gamma\delta) \approx \frac{1}{N_s} \sum_{\xi} R_{\alpha\beta}^{\xi} R_{\gamma\delta}^{\xi} \equiv \langle R_{\alpha\beta} R_{\gamma\delta} \rangle_\xi \tag{10}$$

Calculation of the L_A^ξ terms in eq 9 scales as $O(N_{aux}^2 N_s)$ while the overall computational scaling of the R^ξ matrices is $O(N_s N_{AO}^2 N_{aux})$. This is similar to the deterministic RI components $K_{\alpha\beta}^Q$ and $K_{\gamma\delta}^Q$ but with an additional prefactor of N_s.

The transformation to the MO basis is given by

Table 1. MP2 and sRI−MP2 Parameters and Results for the Water Cluster Test Set (N_e, Number of Correlated Electrons; MP2 and sRI−MP2 Correlation Energies Per Electron in hartree; Error and Standard Error Per Electron in kcal/mol)

N_e	N_{AO}	N_{aux}	MP2	sRI−MP2	error	std error	N_s
64	200	768	−0.0270	−0.0281	0.6750	0.8440	200
168	500	2016	−0.0268	−0.0261	0.3947	0.8422	200
256	800	3072	−0.0268	−0.0269	0.0577	0.6579	200
416	1300	4992	−0.0269	−0.0268	0.0426	1.0825	200
624	1950	7488	−0.0270	−0.0283	0.8304	1.1841	200
888	2775	10656		−0.0281		1.0755	200

$$R^\xi_{p\beta} = \sum_{\alpha}^{N_{AO}} C^p_\alpha R^\xi_{\alpha\beta}$$

$$R^\xi_{pq} = \sum_{\beta}^{N_{AO}} C^q_\beta R^\xi_{p\beta} \tag{11}$$

and is a two-step process with both transformation steps scaling as $O(N_s N^3_{AO})$ compared to the deterministic transformation that costs $O(N_{aux} N^3_{AO})$.

The stochastic error of the elements of the identity matrix and therefore the error of the ERIs is governed by the number of stochastic orbitals, N_s, as can be seen from eq 7. Since it is the *length* of stochastic arrays, N_{aux}, that increases with the system size rather than the number of stochastic orbitals, N_s is expected to have little size dependence. We will show for a set of water clusters that N_s remains approximately constant as a function of system size for a fixed statistical error. Thus, the transformation from the AO to MO basis scales as $O(N^3_{AO})$ and the 4-index ERI assembly as $O(N^4_{AO}$—a factor of N_{aux}/N_s less than deterministic RI.

Stochastic Resolution of Identity MP2. As we have stated above, in some instances the sRI approximation may lead to an additional decrease in scaling due to the decoupling of indices. We now demonstrate this for MP2. The MP2 energy expression for a closed shell system may be written as

$$E_{MP2} = \sum_{abij} \frac{(ai|bj)[2(ai|bj) - (bi|aj)]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{12}$$

Implementing the sRI approximation we obtain a similar expression for sRI−MP2

$$E_{sRI-MP2} = \sum_{abij} \frac{\langle R^\xi_{ai} R^\xi_{bj}\rangle_\xi [2\langle R^\xi_{ai} R^\xi_{bj}\rangle_\xi - \langle R^\xi_{aj} R^\xi_{bi}\rangle_\xi]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{13}$$

Although eq 12 is an $O(N^2_{occ} N^2_{virt})$ step, MP2 scales as $O(N_{occ} N^4_{AO})$ because of the 4-index ERI transformation, while RI-MP2 scales as $O(N^2_{occ} N^2_{virt} N_{aux})$ due to the reconstruction step in eq 4. Similarly, with the naive application of the sRI approximation in eq 13 one sees that sRI−MP2 is expected to scale as $O(N_s N^2_{occ} N^2_{virt})$. However, with the introduction of a *second stochastic orbital* in conjunction with Almlöf's[36] time-integrated decomposition of the energy denominator, it is possible to reduce the overall cost to that of the R matrices (eq 9). First, the sRI−MP2 energy expression is written in terms of *two* rather than one stochastic orbital denoted by ξ and ξ' in eq 14.

$$E_{sRI-MP2} = \left\langle \sum_{abij} \frac{R^\xi_{ai} R^\xi_{bj}[2R^{\xi'}_{ai} R^{\xi'}_{bj} - R^{\xi'}_{aj} R^{\xi'}_{bi}]}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \right\rangle_{\xi\xi'} \tag{14}$$

The introduction of the second stochastic orbital doubles the number of R^ξ matrices while leaving the number of elements in the stochastic average unchanged. The use of two stochastic orbitals is denoted by $\langle ...\rangle_{\xi\xi'}$. The modest increase in the computational prefactor and memory requirements of sRI−MP2 is extremely advantageous as it allows the stochastic average to be taken over the *entire* sRI−MP2 energy expression rather than individual integral pairs, *decoupling* indices in the numerator. The numerator may now be rearranged in terms of products of the form $R^\xi_{ai} R^{\xi'}_{ai}$ and $R^\xi_{ai} R^{\xi'}_{aj}$ and the denominator rewritten as a time integral resulting in the time-integrated sRI−MP2 expression of eq 15.

$$E_{sRI-MP2} = \int_0^\infty \sum_{abij} \langle [2(R^\xi_{ai} R^{\xi'}_{ai})(R^\xi_{bj} R^{\xi'}_{bj})$$
$$- (R^\xi_{ai} R^{\xi'}_{aj})(R^\xi_{bj} R^{\xi'}_{bi})]$$
$$\times e^{-(\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b)t}\rangle_{\xi\xi'}\, dt \tag{15}$$
$$= \int_0^\infty \langle 2A(t)^2 - Tr[E(t)^2]\rangle_{\xi\xi'}\, dt$$

where

$$A(t) = \sum_i^{N_{occ}} \sum_a^{N_{virt}} e^{-(\varepsilon_i - \varepsilon_a)t} R^\xi_{ai} R^{\xi'}_{ai}$$

$$E(t)_{ij} = \sum_a^{N_{virt}} e^{-(\varepsilon_i - \varepsilon_a)t} R^\xi_{ai} R^{\xi'}_{aj} \tag{16}$$

The quantity $A(t)$ scales as $O(N_{occ} N_{virt})$ and the matrix $E(t)$ as $O(N^2_{occ} N_{virt})$. The overall scaling for the energy expression is $O(N_s N_t N^2_{occ} N_{virt})$, where N_t is the number of quadrature points and, in the case of small prefactors, N_s and N_t, becomes $O(N^2_{occ} N_{virt})$.

RESULTS AND DISCUSSION

To study the observed scaling, stochastic errors, and the impact of prefactors N_s and N_t on the sRI−MP2 method, we selected a test set of water clusters consisting of 8, 21, 32, 52, 78, and 111 water molecules. The sRI−ERI and time-integrated sRI−MP2 routines are implemented in a development version of the NWChem 6.6 package of computational chemistry tools.[37] Deterministic MP2 calculations were performed with the NWChem semidirect MP2 module. Dunning's correlation consistent basis sets of double-ζ quality, cc-pVDZ,[38] were used for all calculations, and the corresponding cc-pVDZ-RI auxiliary basis[39,40] was used in sRI−MP2 calculations. Schwartz integral screening was applied to all ERIs. All benchmark calculations were performed with the National Energy Research Scientific Computing Center resource Cori, using a single Haswell compute node and 30 computational cores.

The results are listed in Table 1, where deterministic MP2 and sRI−MP2 correlation energies per electron are given in

hartree and the error in the correlation energy per electron and standard error of correlation energy per electron given in units of kcal/mol. As mentioned previously the computationally demanding step of the sRI approximation is the construction of the R^ξ matrices which scales as $O(N_s N_{AO}^2 N_{aux})$, while the sRI−MP2 energy expression is an $O(N_s N_t N_{occ}^2 N_{virt})$ step. For the given test set 10 quadrature points were found to be sufficient for the energy denominator decomposition. Therefore, the observed scaling of the method is dependent on N_s remaining small with respect to the system size while simultaneously satisfying a standard definition of stochastic convergence. Since the total energy of a system diverges in the thermodynamic limit, we define convergence as a standard error in correlation energy per electron of less than 1.5 kcal/mol per electron. (The standard error of the total energy and the correlation energy are equal.) The results listed in Table 1 show that $N_s = 200$ is sufficient to produce standard errors below 1.5 kcal/mol per electron for all systems within the test set.

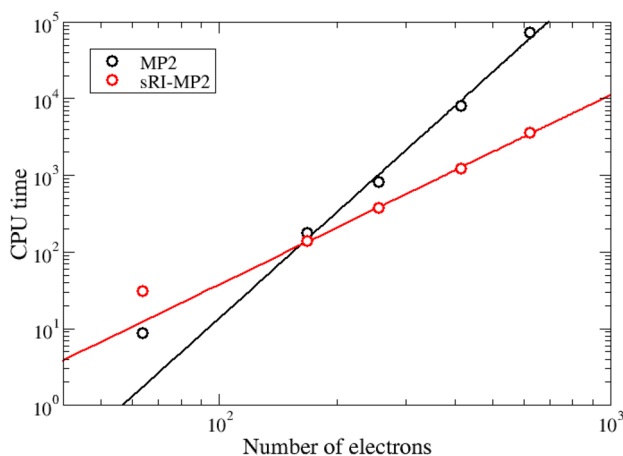The observed MP2 and sRI−MP2 timings per core are plotted in Figure 1. For a system of 8 water molecules the sRI-

Figure 1. Observed MP2 and sRI−MP2 CPU timings per core for the water cluster test set with $N_s = 200$ and a maximum standard error of 1.2 kcal/mol per electron.

MP2 method is 3.5 times more expensive than the deterministic MP2. However, for systems above 161 correlated electrons (approximately 21 water molecules with $N_e = 168$) the computational cost of sRI−MP2 drops below that of MP2 with an observed scaling of $O(N_e^{2.4})$, where N_e is the number of correlated electrons.

If the extent of the sRI−MP2 capabilities were limited to converging the correlation energy per electron to within a given threshold of the deterministic results, sRI−MP2 would be of limited utility as in most practical applications it is necessary to

accurately calculate relative energies and forces along the potential energy surface. As an initial investigation we verify that using a standard error of 1.5 kcal/mol per electron as a convergence criterion leads to systematic behavior in the standard errors of the forces as a function of system size. In the 8, 21, 32, 52, and 78 water clusters a central hydrogen-bound pair was selected and numerical forces, with a displacement step of 0.01 bohr, were calculated at five intermolecular distances along the hydrogen-bond coordinate. All other degrees of freedom were fixed in an attempt to avoid any fortuitous error cancelation in the relative total energies.

The absolute and standard errors in the forces with $N_s = 200$ are listed in Table 2. The results show that the absolute errors in the forces at each point are within the standard error and that the standard error increases slowly with system size. Since the scaling of sRI−MP2 depends linearly on the number of stochastic orbitals, a modest increase in computational cost is expected in order to achieve a constant standard error. Recently, it has been shown that correct *ab initio* Langevin dynamics may be performed with stochastic density functional theory with the standard error in the forces being in excess of 10 (kcal/mol)/Å.[41] Selecting a constant standard error of 5 (kcal/mol)/Å for the 21, 32, 52, and 78 water clusters we obtain an observed scaling of $O(N_e^{3.1})$; see Figure 2.
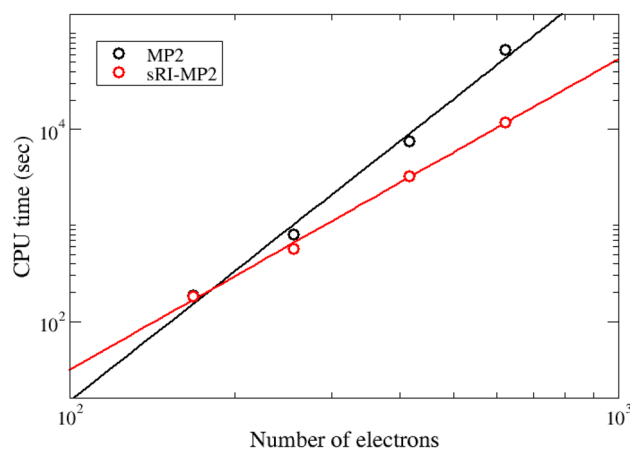

Figure 2. MP2 and sRI−MP2 CPU timings per core for the 21, 32, 52, and 78 water cluster test set with a constant standard error in the forces of 5 (kcal/mol)/Å.

To conclude, we introduced a stochastic implementation of the resolution of identity approximation that reduced the scaling of the deterministic AO to MO transformation from $O(N_{AO}^5)$ (or $O(N_{AO}^4)$ for the deterministic RI approximation) to $O(N_{AO}^3)$ and overall memory requirements to $O(N_{AO}^2)$. It was then demonstrated that, with the introduction of an additional stochastic orbital, the stochastic averaging may take place over

Table 2. Absolute and Standard Error in sRI−MP2 Forces at Five Points along a Hydrogen-Bond Coordinate in the 8, 21, 32, 52, and 78 Water Clusters (N_e, Number of Correlated Electrons; r_i, ith Hydrogen-Bond Distance; Absolute and Standard Errors in (kcal/mol)/Å; Standard Errors in Parentheses)

N_e	r_1	r_2	r_3	r_4	r_5
64	0.43 (3.66)	2.17 (2.84)	1.00 (2.55)	0.17 (2.62)	1.51 (2.82)
168	4.09 (7.65)	3.76 (6.66)	2.02 (5.74)	1.27 (4.98)	1.31 (4.77)
256	5.06 (8.38)	1.27 (7.34)	0.12 (5.85)	0.71 (4.78)	0.04 (4.78)
416	7.35 (9.91)	1.62 (9.07)	1.61 (8.05)	1.27 (7.30)	0.64 (7.18)
624	1.01 (11.01)	4.39 (9.04)	3.23 (8.66)	0.47 (9.03)	3.03 (9.21)

more complex expressions rather than individual 4-index ERIs, leading to a *decoupling* of indices. This led to the time-integrated sRI−MP2 with a formal scaling of $O(N_{AO}^3)$. When applied to a set of *three-dimensional* systems, scalings of $O(N_e^{2.4})$ and $O(N_e^{3.1})$ were observed when maintaining a constant error in the energy per electron and total forces, respectively. Given that 4-index ERIs are ubiquitous in *ab initio* electronic structure methods, we expect the sRI approximation to be widely applicable and readily interfaced with other reduced scaling techniques.

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Notes
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