

Linear and sublinear scaling formation of Hartree–Fock-type exchange matrices

Christian Ochsenfeld, Christopher A. White, and Martin Head-Gordon

Citation: *J. Chem. Phys.* **109**, 1663 (1998); doi: 10.1063/1.476741

View online: <http://dx.doi.org/10.1063/1.476741>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v109/i5>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



**ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.**

[LEARN MORE](#)

Linear and sublinear scaling formation of Hartree–Fock-type exchange matrices

Christian Ochsenfeld, Christopher A. White, and Martin Head-Gordon

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

(Received 12 November 1997; accepted 21 April 1998)

We present a new method (LinK) to form the exact exchange matrix, as needed in Hartree–Fock and hybrid density functional theory calculations, with an effort capable of scaling only linearly with molecular size. It preserves the highly optimized structure of conventional direct self-consistent field (SCF) methods with only negligible prescreening overhead and does not impose predefined decay properties. Our LinK method leads to very early advantages as compared to conventional methods for systems with larger band gaps. Due to negligible screening overhead it is also competitive with conventional SCF schemes both for small molecules and systems with small band gaps. For the formation of an exchange-type matrix in coupled perturbed SCF theory our LinK method can exhibit sublinear scaling, or more precisely, independence of the computational effort from molecular size. © 1998 American Institute of Physics. [S0021-9606(98)00229-3]

I. INTRODUCTION

Modern *ab initio* electronic structure methods are currently confined to molecules in the 100 atom regime. To allow for the treatment of larger molecular systems it is crucial to exploit any locality of electronic structure and, in this way, improve the scaling behavior of such methods. These improvements will allow for a theoretical investigation of molecules unprecedented in size, such as biomolecules, an area which has been so far limited to the application of semi-empirical or force-field approaches. However, since the reliability of these methods is unclear and they do not offer the possibility to systematically improve the level of accuracy, it is highly desirable to apply reliable *ab initio* methods to these chemical problems. In this way, it will be possible to check simple model ideas and establish new ones to gain a better understanding of, for example, biochemical processes.

The standard self-consistent field (SCF) methods of quantum chemistry such as density functional theory (DFT) and Hartree–Fock (HF) theory consist of two computationally demanding pieces (e.g., Refs. 1–3): first, the formation of the Fock matrix, which conventionally scales quadratically with molecular size (M); second, the density update of the self-consistent field (SCF) approximation which is conventionally done as a diagonalization, scaling cubically with molecular size. However, the latter step shows a very small prefactor and therefore only becomes important for very large systems. In addition, numerous diagonalization-free methods have been proposed to avoid this potential bottleneck (see for example Refs. 4–6 and references therein).

The formation of the Fock matrix itself involves two computationally expensive parts: Coulomb (**J**) and exchange (**K**) terms. For the so-called Coulomb problem, highly effective linear scaling methods have been introduced (e.g., Refs. 7–12 and references therein). In DFT methods, evaluation of the exchange (and correlation) contributions to the Fock matrix via numerical quadratures is well established as scaling linearly (e.g., Refs. 13 and 14 and references therein) with

molecular size. The other types of terms which often enter the Fock matrix are the so-called exact exchange contributions, as needed both within conventional Hartree–Fock theory, and popular hybrid DFT methods such as B3PW91 and B3LYP.¹⁵ Recently, several approaches to reduce the computational scaling properties of exact exchange evaluation have been introduced.^{16–18} The purpose of this paper is to present a new scheme for exact exchange, which offers important advantages relative to earlier algorithms.

The first two linear-scaling methods for exact exchange both required assumptions about the long-range density and exchange behavior,^{16,17} which means that they could not readily ensure a prescribed accuracy. This difficulty was overcome in the recently proposed ONX (order N exchange) algorithm, of Schwegler *et al.*¹⁸ by employing traditional SCF density-weighted integral estimates^{1–3} of exchange within a novel loop structure. For insulators this achieves effective linear scaling by using preordered integral estimates, which allow leaving a loop early and therefore avoid unnecessary computational effort. For small-gap systems with long-range exchange contributions, ONX¹⁸ reverts back to quadratic scaling with molecular size. This novel loop structure (Fig. 4 in Ref. 18), designed specifically for exchange, also potentially allows efficiency improvements based on customizing the associated integral code for exchange. However, unlike conventional direct SCF,^{1–3} it does not exploit permutational symmetry of the two-electron integrals. In this way, ONX¹⁸ suffers a formal performance loss of a factor of four in the rate-determining integral evaluation as compared to conventional quadratically scaling exchange-only algorithms.

In this paper we present a new effective linear scaling method for the calculation of the exact exchange matrix associated with a determinant whose one particle density matrix is **P**,

$$K_{\lambda\sigma} = P_{\mu\nu} \cdot (\mu\lambda|\nu\sigma). \quad (1)$$

Like Ref. 18, our new method does not require any assumptions about decay properties of the density matrix \mathbf{P} , but by contrast we still exploit permutational symmetry in the integral evaluation. The proposed screening scheme requires little overhead, and in this way gives the earliest possible crossover (or advantage) relative to conventional methods (at least without customizing the integral evaluation methods specifically for exchange). Also, as a result, our new method is very competitive with $\mathcal{O}(M^2)$ schemes even for small molecules and systems with small band gaps.

Our new method, which we denote as LinK (Linear exchange K), is motivated by two objectives. The first is to exploit the full permutational symmetry of the two-electron integrals and preserve the integral-driven structure of conventional SCF methods. The second is to exploit ordering ideas of ONX,¹⁸ but subject to achieving the first objective. For the final threshold criterion we use the integral estimates of Häser and Ahlrichs³ of conventional direct SCF methods, similar to ONX,¹⁸ and separate screening from integral evaluation. In the current implementation we completely separate the formation of exact exchange from the Coulomb interactions, since in this way highly efficient methods for the construction of the Coulomb matrix such as the J -engine¹⁹ and the CFMM (continuous fast multipole method)^{7,8} can be employed. However, this total separation is not a necessary requirement of our LinK method, and some of the integrals can be reused for the \mathbf{J} -part.

Our LinK method not only yields exact exchange matrices with linear scaling effort for large-gap systems, but also reduces the scaling properties to sublinear for the exchange-type contraction of a local density derivative (with respect to nuclear displacements) matrix with two-electron integrals. Such contractions are necessary for solving the coupled-perturbed SCF (CPSCF) equations which have been recently reformulated by Ochsenfeld and Head-Gordon⁶ in a fully local density matrix-based scheme (D-CPSCF). This D-CPSCF formulation exploits the strong locality of the density derivative matrix to reduce the $\mathcal{O}(M^4)$ scaling to asymptotically linear, which is not possible in conventional AO-based (atomic orbital based) CPSCF schemes (e.g., Refs. 20–22).

II. DESCRIPTION OF THE LINK METHOD

With the introduction of direct SCF methods the screening with thresholds of insignificant elements by using density-weighted integral estimates^{1–3} became an important aspect. Conventional schemes form Coulomb and exchange parts simultaneously using screening based on maximum density-matrix elements over the different contributions to select significant shell quartets. This selection procedure is intrinsically $\mathcal{O}(M^2)$, and additionally the Coulomb contribution is quadratic when evaluated in terms of two-electron integrals. Exchange itself involves only a linear number of significant terms for large molecules with large band gaps, and thus the scaling behavior of exchange-only terms (if separated from Coulomb terms) is limited by the $\mathcal{O}(M^2)$ screening. Therefore it is crucial to formulate the screening procedure in a linear fashion to achieve linear scaling for the formation of the exact exchange matrix.^{16–18} Although the screening normally shows a quite small prefactor, it becomes

```

Loop over types (angular momenta, contraction,...) of shell-pair blocks
Pre-ordering and pre-selection to find significant elements in  $P_{\mu\nu}$ :
Loop over all  $\mu$ 's in significant "bra"-shell pairs
  Loop over all  $\nu$ 's in significant "ket"-shell pairs
    if  $([P_{\mu\nu} \cdot (\mu_{\max}|\mu_{\max})^{1/2} \cdot (\nu_{\max}|\nu_{\max})^{1/2}] > \text{Threshold})$  then
      Store significant  $\nu$ 's for each  $\mu$ 
    endif
  endloop
  Sort  $\nu$ 's by size of  $[|P_{\mu\nu}| \cdot (\nu_{\max}|\nu_{\max})^{1/2}]$  for each  $\mu$ 
endloop
Loop over significant "bra"-shell pairs  $\mu\lambda$ 
  Formation of significant shell-pair list ML:
  Loop over significant  $\nu$ 's corresponding to  $\mu$ 
    Loop over significant  $\sigma$ 's
      if  $([|P_{\mu\nu}| \cdot (\mu\lambda|\mu\lambda)^{1/2} \cdot (\nu\sigma|\nu\sigma)^{1/2}] > \text{Threshold})$  then
        Add  $(\nu\sigma)$  to  $ML_\mu$ 
      else: Leave  $\sigma$ -loop
    endloop
    If resulting number of  $\sigma$ 's in  $ML_\mu$  is zero then: Leave  $\nu$ -loop
  endloop
  Same loop for  $\lambda$  to form  $ML_\lambda$ 
  Merging sorted shell-pair lists  $ML_\mu$  and  $ML_\lambda$  yields ML
  Loop over significant "ket"-shell pairs  $\nu\sigma \in ML$ 
    Form  $(\mu\lambda|\nu\sigma)$  and contract with  $P_{\mu\nu}$ ,  $P_{\mu\sigma}$ ,  $P_{\lambda\nu}$ , and  $P_{\lambda\sigma}$ 
  endloop
endloop
endloop

```

FIG. 1. Outline of the LinK algorithm which preserves the integral-driven structure of highly optimized standard SCF programs and ensures full exploitation of permutational symmetry. Notation and scaling properties are described in the text.

important for large systems and especially for the formation of exchange-type matrices involving local quantities (e.g., derivative density matrices), where the screening dominates the calculation at a much earlier stage.

Our new LinK method, which can achieve linear and sublinear scaling for exact exchange-type matrices, is outlined in Fig. 1. The possibility of sublinear scaling of the LinK method for contraction of local matrices, important in the D-CPSCF method,⁶ is described later in this paper. The LinK method can be viewed as involving three pieces: First, the preordering and preselection part, second, the formation of significant shell-pair listings (denoted as minilist, ML, in Fig. 1) (note that in the present implementation only one final ML and an N^2 \mathbf{K} -storage is used. Although this is not important even for very large systems, it can be easily avoided. To ensure the formation directly into a sparse \mathbf{K} , four minilists are required, which is only a trivial extension of the algorithm depicted in Fig. 1) controlling which integrals have to be evaluated, and third, integral construction itself, and formation of the exchange matrix contributions. For the integral prescreening, the estimate introduced by Häser and Ahlrichs³ is used,

$$|(\mu\lambda|\nu\sigma)| \leq (\mu\lambda|\mu\lambda)^{1/2} \cdot (\nu\sigma|\nu\sigma)^{1/2}. \quad (2)$$

The first part of LinK depicted in Fig. 1 serves to select for each μ contained in the "bra"-shell pair, which ν 's of the "ket"-shell pair are significant. Within the outside loop over different types of shell pairs (angular momenta, contraction,...) the following criterion is used:

$$|P_{\mu\nu}| \cdot (\mu_{\max}|\mu_{\max})^{1/2} \cdot (\nu_{\max}|\nu_{\max})^{1/2}. \quad (3)$$

Here $(\mu_{\max}|\mu_{\max})^{1/2}$ denotes the maximum over all integral estimates of this shell-pair type, $(\mu\lambda|\mu\lambda)^{1/2}$, that involve shell μ . Note that before starting with the loop structure de-

TABLE I. Timings and relative energy deviations for linear alkanes, C_nH_{2n+2} (6-31G*), comparing standard SCF (STD) with LinK and CFMM. In addition, we display data for a quadratically scaling HF exchange-only algorithm (CPU_K). Relative deviations are given with respect to the absolute energy value as obtained with STD and 10^{-10} threshold. All CPU timings are in seconds.

Molecule	Method	Thresh	E_{total}	CPU_{total}	E_K	CPU_{LinK}	CPU_K	E_J	CPU_J
$C_{15}H_{32}$	STD	10^{-10}	-586.662 223	297	-89.286 737	1203.798 901	...
		10^{-8}	$1.4 \cdot 10^{-7}$	238	$5.5 \cdot 10^{-8}$	$5.4 \cdot 10^{-7}$...
		10^{-7}	$1.2 \cdot 10^{-6}$	204	$3.2 \cdot 10^{-8}$	$3.2 \cdot 10^{-7}$...
		10^{-6}	$1.6 \cdot 10^{-4}$	164	$1.3 \cdot 10^{-5}$	$9.2 \cdot 10^{-4}$...
	LinK /CFMM	10^{-8}	$5.9 \cdot 10^{-7}$	252	$1.0 \cdot 10^{-8}$	176	177	$6.0 \cdot 10^{-7}$	76
		10^{-7}	$3.1 \cdot 10^{-6}$	208	$3.5 \cdot 10^{-6}$	143	143	$4.1 \cdot 10^{-7}$	65
		10^{-6}	$9.4 \cdot 10^{-4}$	153	$1.7 \cdot 10^{-5}$	100	102	$9.2 \cdot 10^{-4}$	53
$C_{30}H_{62}$	STD	10^{-10}	-1172.163 632	1411	-177.917 118	2922.179 584	...
		10^{-8}	$2.1 \cdot 10^{-7}$	1111	$1.2 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$...
		10^{-7}	$2.1 \cdot 10^{-6}$	950	$1.1 \cdot 10^{-7}$	$2.9 \cdot 10^{-6}$...
		10^{-6}	$4.0 \cdot 10^{-4}$	745	$3.2 \cdot 10^{-5}$	$2.8 \cdot 10^{-3}$...
	LinK /CFMM	10^{-8}	$1.3 \cdot 10^{-6}$	744	$6.5 \cdot 10^{-8}$	570	574	$1.4 \cdot 10^{-6}$	174
		10^{-7}	$5.0 \cdot 10^{-6}$	549	$8.3 \cdot 10^{-6}$	402	418	$3.2 \cdot 10^{-6}$	147
		10^{-6}	$2.8 \cdot 10^{-3}$	381	$1.8 \cdot 10^{-5}$	260	277	$2.8 \cdot 10^{-3}$	121
$C_{60}H_{122}$	STD	10^{-10}	-2343.166 448	6599	-355.177 882	6913.992 108	...
		10^{-8}	$3.5 \cdot 10^{-7}$	5142	$2.5 \cdot 10^{-7}$	$2.8 \cdot 10^{-6}$...
		10^{-7}	$3.9 \cdot 10^{-6}$	4344	$2.6 \cdot 10^{-7}$	$9.0 \cdot 10^{-6}$...
		10^{-6}	$8.8 \cdot 10^{-4}$	3349	$7.0 \cdot 10^{-5}$	$7.3 \cdot 10^{-3}$...
	LinK /CFMM	10^{-8}	$3.1 \cdot 10^{-6}$	1799	$1.9 \cdot 10^{-7}$	1426	1493	$3.3 \cdot 10^{-6}$	373
		10^{-7}	$7.8 \cdot 10^{-6}$	1297	$1.8 \cdot 10^{-5}$	983	1054	$9.7 \cdot 10^{-6}$	314
		10^{-6}	$7.3 \cdot 10^{-3}$	861	$4.3 \cdot 10^{-5}$	605	670	$7.3 \cdot 10^{-3}$	256

scribed in Fig. 1, the significant shell pairs have been preselected by using overlap criteria and preordered by size of the integral estimate—which is already done in the conventional SCF code of the *Q-Chem* package²³ into which we implemented our new LinK method. After all significant ν 's for a given μ have been evaluated, the ν 's are ordered by the size of density-weighted integral estimates,

$$|P_{\mu\nu}| \cdot (\nu_{\max}|\nu_{\max})^{1/2}. \quad (4)$$

This density-weighted integral ordering in LinK will allow immediate loop exits once a certain threshold criterion is reached, and is crucial to permit linear scaling. A preordering of integral estimates was the key point in the ONX method.¹⁸

The first part of the LinK loop reaches exact linear scaling once a density increases linearly with the system size. [This is also true for the ONX scheme (Ref. 18), although Figs. 3 and 4 of Ref. 18 show an explicit $\mathcal{O}(M^2)$ loop with no jump-out. In practice this $\mathcal{O}(M^2)$ structure can be replaced by looping over significant density elements only, so that once a linearly increasing density is given, a linear scaling algorithm is reached.] However, since the prefactor of this step is extremely small, the second part of the LinK algorithm determines if and when effective linear scaling can be observed. In this second step, the significant shell-pair list is formed by using the following screening criterion:

$$|P_{\mu\nu}| \cdot (\mu\lambda|\mu\lambda)^{1/2} \cdot (\nu\sigma|\nu\sigma)^{1/2}. \quad (5)$$

The “ ν ”-ordering and the overall shell-pair ordering allow leaving the ν - and the σ -loop of Fig. 1 immediately once a certain threshold criterion is met. In this way the screening is cheap and the second part of LinK reaches linear scaling with system size once the final number of shell-quartets that contributes significantly to the exchange matrix scales linearly. Not only effective linear scaling but also true

asymptotic linear scaling (not only in the rate-determining step) will be reached if the density matrix itself is also scaling in such a way.

III. DISCUSSION

A. Performance of the LinK method

In the following we will discuss some timings for our new LinK method and the scaling behavior of the method. We will restrict our discussion to three kinds of molecules:²⁴ the same water clusters (3-21G basis) as used by Schwegler *et al.*,¹⁸ graphitic sheets (3-21G; but not the same coordinates as those of Ref. 18), and linear alkanes (6-31G*). To eliminate influences of initial guess behavior, variable thresholds, SCF convergence properties, and incremental Fock builds, we will focus on timings for the formation of only one exact exchange matrix using the same converged density matrix for all different thresholds [root-mean-square (RMS)-error less than 10^{-9}]. To ensure a fair comparison against the standard SCF code for exact exchange we use the same integral package and try to compare similar accuracies in the energy. All converged density matrices are from Hartree–Fock (HF) calculations. All timings were obtained using a development version of the *Q-Chem* program package²³ on a DEC 6000 (266 MHz Alpha 21164 processor) uniprocessor workstation.

Tables I and II display timings for our LinK method as compared to standard SCF code for linear alkanes and water clusters. Comparing quadratic HF exchange-only (CPU_K) and LinK (CPU_{LinK}) shows that screening is not dominant over a wide range (if an efficient quadratic screening is implemented): The maximum win for $C_{60}H_{122}$ using a 6-31G* basis is roughly 10% and for $(H_2O)_{150}$ (3-21G) up to a factor of 1.6 speed-ups can be observed. This emphasizes

TABLE II. Timings and relative energy deviations for water clusters, $(\text{H}_2\text{O})_n$ (3-21G), comparing standard SCF (STD) with LinK and CFMM. In addition, we display data for a quadratically scaling HF exchange-only algorithm (CPU_K). Relative deviations are given with respect to the absolute energy value as obtained with STD and 10^{-10} threshold. All CPU timings are in seconds.

Molecule	Method	Thresh.	E_{total}	$\text{CPU}_{\text{total}}$	E_K	CPU_{LinK}	CPU_K	E_J	CPU_J
$(\text{H}_2\text{O})_{50}$	STD	10^{-10}	-3780.214 411	805	-448.394 164	12 480.309 776	...
		10^{-8}	$5.8 \cdot 10^{-7}$	482	$5.3 \cdot 10^{-7}$	$1.2 \cdot 10^{-6}$...
		10^{-7}	$2.9 \cdot 10^{-6}$	355	$6.2 \cdot 10^{-7}$	$2.5 \cdot 10^{-5}$...
		10^{-6}	$9.4 \cdot 10^{-6}$	244	$3.3 \cdot 10^{-5}$	$5.8 \cdot 10^{-4}$...
	LinK /CFMM	10^{-8}	$3.0 \cdot 10^{-6}$	308	$1.8 \cdot 10^{-6}$	152	156	$1.2 \cdot 10^{-6}$	156
		10^{-7}	$4.4 \cdot 10^{-5}$	205	$1.9 \cdot 10^{-5}$	88	97	$2.5 \cdot 10^{-5}$	117
		10^{-6}	$8.1 \cdot 10^{-4}$	131	$2.3 \cdot 10^{-4}$	46	56	$5.9 \cdot 10^{-4}$	85
$(\text{H}_2\text{O})_{100}$	STD	10^{-10}	-7560.739 594	4755	-896.759 517	38 300.250 000	...
		10^{-8}	$2.2 \cdot 10^{-6}$	2718	$1.1 \cdot 10^{-6}$	$6.0 \cdot 10^{-6}$...
		10^{-7}	$7.4 \cdot 10^{-6}$	1928	$1.7 \cdot 10^{-6}$	$8.0 \cdot 10^{-5}$...
		10^{-6}	$2.9 \cdot 10^{-5}$	1288	$7.0 \cdot 10^{-5}$	$1.8 \cdot 10^{-3}$...
	LinK /CFMM	10^{-8}	$1.1 \cdot 10^{-5}$	1048	$4.6 \cdot 10^{-6}$	541	610	$5.8 \cdot 10^{-6}$	507
		10^{-7}	$1.3 \cdot 10^{-4}$	671	$5.0 \cdot 10^{-5}$	293	357	$8.0 \cdot 10^{-5}$	378
		10^{-6}	$2.4 \cdot 10^{-3}$	405	$5.7 \cdot 10^{-4}$	138	198	$1.8 \cdot 10^{-3}$	267
$(\text{H}_2\text{O})_{150}$	STD	10^{-10}	-11 341.127 919	12374	-1345.167 656	73 741.059 945	...
		10^{-8}	$4.1 \cdot 10^{-6}$	6858	$1.6 \cdot 10^{-6}$	$1.7 \cdot 10^{-5}$...
		10^{-7}	$1.1 \cdot 10^{-5}$	4899	$2.5 \cdot 10^{-6}$	$9.3 \cdot 10^{-5}$...
		10^{-6}	$9.9 \cdot 10^{-5}$	3179	$1.1 \cdot 10^{-4}$	$4.9 \cdot 10^{-3}$...
	LinK /CFMM	10^{-8}	$2.4 \cdot 10^{-5}$	1907	$7.5 \cdot 10^{-6}$	1035	1261	$1.6 \cdot 10^{-5}$	872
		10^{-7}	$1.7 \cdot 10^{-4}$	1176	$7.8 \cdot 10^{-5}$	541	746	$9.3 \cdot 10^{-5}$	635
		10^{-6}	$5.7 \cdot 10^{-3}$	715	$8.5 \cdot 10^{-4}$	251	413	$4.9 \cdot 10^{-3}$	464

that one cannot afford any loss of performance in the rate-determining evaluation of the two-electron integrals and their contraction with density-matrix elements.

In Figs. 2 and 3 overall timings of standard SCF and the combination of LinK and CFMM are compared using a threshold of $10^{-7}/10^{-8}$. The speed-ups for our LinK/CFMM scheme for $\text{C}_{60}\text{H}_{122}$ are 3.3 and for $(\text{H}_2\text{O})_{150}$ 2.6 versus standard total HF, if one compares similar accuracies (see Tables I and II). These quite large speed-ups obtained by using LinK and CFMM together are primarily a result of separating Coulomb and exchange evaluation and using linear scal-

ing methods for the former, although the value of the LinK method increases steadily as system size increases.

It is worthwhile to point out that the scaling behavior for the HF exchange formation for water clusters and linear alkanes is quite similar to the behavior of important elements in the density matrix. We believe that in general the best way of understanding the scaling behavior, influenced directly by the density, is to investigate the way the number of significant elements increases with system size, instead of judging by observing the overall sparsity. A linear or near-linear scaling growth of this number is reached significantly earlier

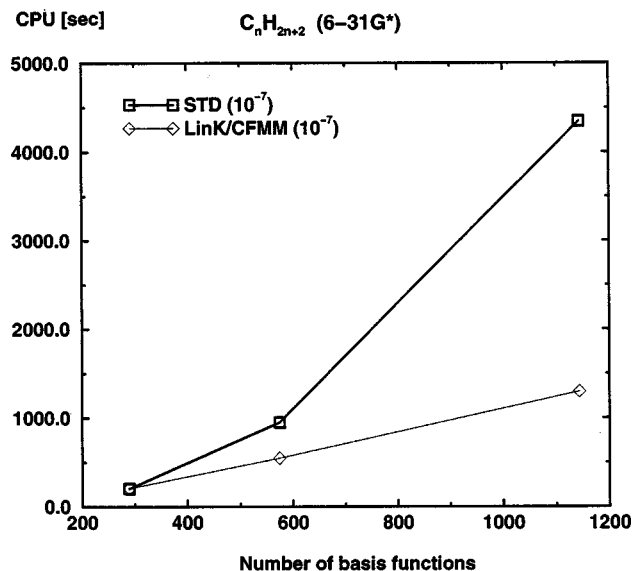


FIG. 2. Scaling behavior of total Fock builds using standard HF (STD) as compared to the combination of LinK/CFMM for linear alkanes $\text{C}_n\text{H}_{2n+2}$ (6-31G*; see Table I).

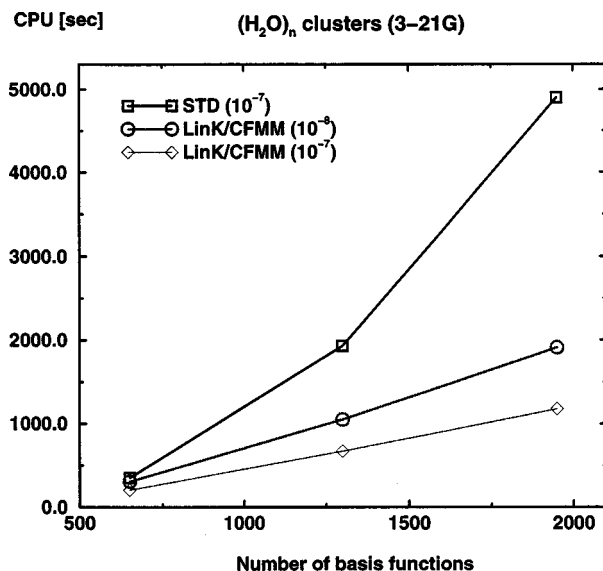


FIG. 3. Scaling behavior of total Fock builds using standard HF (STD) as compared to the combination of LinK/CFMM for water clusters $(\text{H}_2\text{O})_n$ (3-21G; see Table II).

TABLE III. Timings and relative energy deviations for graphitic sheets, $C_{6n}H_{6n}$ (3-21G), comparing standard SCF (STD) with LinK and CFMM. Relative deviations are given with respect to the absolute energy value as obtained with STD and 10^{-10} threshold. All CPU timings are in seconds.

Method	Molecule	Thresh.	E_{total}	CPU _{total}	E_K	CPU _{LinK}	E_J	CPU _J
STD	$C_{24}H_{12}$	10^{-10}	-910.785 809	182	-128.042 154	...	2252.342 833	...
		10^{-7}	$3.8 \cdot 10^{-5}$	114	$4.1 \cdot 10^{-6}$...	$2.8 \cdot 10^{-4}$...
	$C_{54}H_{18}$	10^{-10}	-2044.138 252	1633	-285.297 676	...	7385.843 096	...
		10^{-7}	$2.4 \cdot 10^{-4}$	903	$3.0 \cdot 10^{-5}$...	$2.7 \cdot 10^{-3}$...
	$C_{96}H_{24}$	10^{-10}	-3629.471 145	7026	-504.702 674	...	17 264.636 061	...
		10^{-7}	$5.7 \cdot 10^{-4}$	3669	$7.9 \cdot 10^{-5}$...	$8.4 \cdot 10^{-3}$...
LinK /CFMM	$C_{24}H_{12}$	10^{-8}	$1.1 \cdot 10^{-5}$	142	$1.1 \cdot 10^{-6}$	106	$1.2 \cdot 10^{-5}$	36
		10^{-6}	$5.3 \cdot 10^{-4}$	88	$1.1 \cdot 10^{-5}$	63	$5.2 \cdot 10^{-4}$	25
	$C_{54}H_{18}$	10^{-8}	$7.4 \cdot 10^{-5}$	914	$3.2 \cdot 10^{-6}$	777	$7.7 \cdot 10^{-5}$	137
		10^{-6}	$1.7 \cdot 10^{-3}$	484	$3.3 \cdot 10^{-5}$	398	$1.7 \cdot 10^{-3}$	86
	$C_{96}H_{24}$	10^{-8}	$2.3 \cdot 10^{-4}$	3198	$6.9 \cdot 10^{-6}$	2868	$2.4 \cdot 10^{-4}$	330
		10^{-6}	$7.2 \cdot 10^{-4}$	1554	$5.1 \cdot 10^{-5}$	1357	$6.7 \cdot 10^{-4}$	197

than a pronounced overall sparsity: *The way the number of significant elements increases determines if the computational effort scales linearly; the sparsity influences the prefactor for the scaling.*

For small molecules, the LinK method involves almost exactly the same computational effort as a conventional exchange-only scheme, and becomes superior with increasing molecular size if screening becomes important in those. For molecules with small band gaps where this is not the case, LinK reverts back to the conventional quadratic scaling with only negligible screening overhead. Such data are shown in Table III for graphitic sheets up to $C_{96}H_{24}$. Here LinK shows almost exactly the same timings as exchange-only HF (data are not listed in Table III, since deviations are negligible—less than 1%). However, due to the favorable linear scaling properties of the CFMM method⁷⁻⁹ for the Coulomb part, it is still possible to achieve speed-ups of more than a factor of two in computational costs as compared to conventional simultaneous **J** and **K** formation (Note: we compare similar errors in the final energy; due to the more favorable computational effort of CFMM in the case of graphitic sheets, one can use higher accuracy in the **J** part). In other words, even in a case like this where the density matrix is delocalized, the exchange-only screening is substantially more powerful than combined Coulomb/exchange screening as used in conventional SCF calculations.

We note that the timings presented above represent worst cases for the molecules studied, in the sense that we have deliberately excluded the speed-ups obtainable from using incremental Fock builds, lower integral tolerances in early SCF iterations, and the like. While this makes the comparisons against a simple evaluation of exact exchange very clear, one will want to exploit all of these well-established tricks (e.g. Ref. 3) in production calculations using the LinK method. Indeed, illustrative ONX calculations¹⁸ have already shown the substantial performance improvements that can be obtained in this way within a linear scaling Fock construction scheme, which also allows full exploitation of density-matrix sparsity.

Finally, a very important application of our LinK

method is the exchange-type contraction of a density-matrix derivative with respect to nuclear displacements. In this case, application of LinK permits a reduction of computational effort such that the scaling properties approach being independent of system size for one perturbation.⁶ This is substantiated by the data displayed in Table IV and Fig. 4, corresponding to the exchange-type contraction of one representative local matrix

$$(\mathbf{P}^x \mathbf{S} \mathbf{P} + \mathbf{P} \mathbf{S}^x - 2 \mathbf{P} \mathbf{S}^x \mathbf{P}), \quad (6)$$

which is a rate-determining step in solving the D-CPSCF equations of Ochsenfeld and Head-Gordon.⁶ LinK is already for $C_{50}H_{102}$ (6-31G*) up to a factor of 2.3 faster than conventional exact exchange. Although the absolute time effort for this contraction step seems to be very small (see Table IV), it has to be remembered that it is done (3* number of atoms) times, and thereby becomes highly significant.

B. Comparison of the LinK and ONX methods

We do not attempt any comparison against earlier linear scaling exchange methods that do not yield bounded errors, such as ONX-A¹⁶ and NFX.¹⁷ The most interesting compari-

TABLE IV. Formation of local exchange-type matrices as occurring in D-CPSCF theory [see text and Eq. (6)]. We compare timings using a standard HF exchange-only routine vs LinK for linear alkanes, C_nH_{2n+2} (6-31G*). All CPU timings are in seconds.

Molecule	Thresh.	Δ_K^a	CPU _{LinK}	CPU _{K-only STD}
$C_{15}H_{32}$	10^{-7}	$2.3 \cdot 10^{-6}$	58	62
	10^{-6}	$2.7 \cdot 10^{-5}$	27	30
	10^{-5}	$2.2 \cdot 10^{-4}$	10	12
$C_{30}H_{62}$	10^{-7}	$2.3 \cdot 10^{-6}$	76	89
	10^{-6}	$2.7 \cdot 10^{-5}$	31	40
	10^{-5}	$2.1 \cdot 10^{-4}$	12	17
$C_{40}H_{82}$	10^{-7}	$2.3 \cdot 10^{-6}$	80	103
	10^{-6}	$2.7 \cdot 10^{-5}$	33	47
	10^{-5}	$2.1 \cdot 10^{-4}$	13	23
$C_{50}H_{102}$	10^{-5}	$2.2 \cdot 10^{-4}$	13	30

^aMaximum difference element as compared to the matrix evaluated using a standard SCF with threshold 10^{-10} .

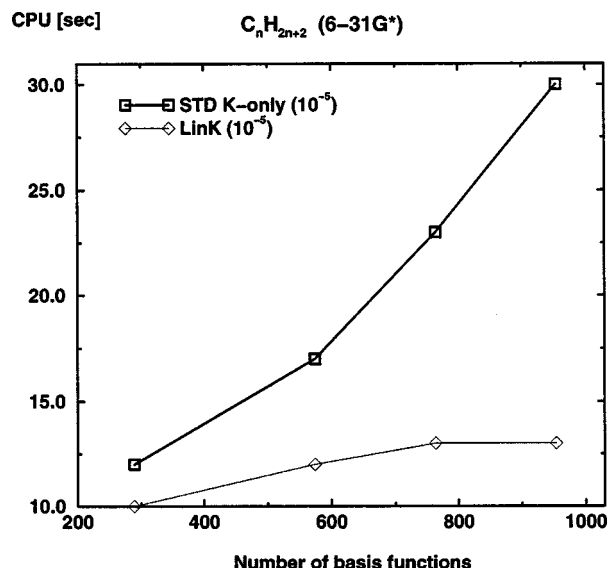


FIG. 4. Formation of local exchange-type matrices as occurring in D-CPSCF theory for linear alkanes, C_nH_{2n+2} , using a 6-31G* basis [see text, Eq. (6), and Table IV].

son is against the ONX method,¹⁸ which also yields bounded errors, but adopts a much different strategy by using new integral evaluation loops that do not exploit permutational symmetry.

We cannot meaningfully compare CPU times against ONX because we cannot separate differences in the speed of the (different) underlying integral codes from differences arising from the different treatment of permutational symmetry. Instead, we can begin a comparison by first assessing the extent to which permutational symmetry is preserved for nonzero exchange interactions in very large molecules. This can be done by evaluating the ratio of the number of nonzero exchange interactions to the number of integrals required to evaluate those interactions, yielding a result between 1 (no permutational symmetry) and 4 (full permutational symmetry). The larger the ratio, the greater the value of exploiting permutational symmetry, in the LinK method. For the molecules considered in this section, the effective permutational factor is between 2.9 and 3.6 for linear alkanes (depending on thresholds), 2.7 to 3.0 for the water clusters, and 3.4 and higher for graphitic sheets. This behavior is roughly independent of molecule size.

The underlying reason why significant permutational factors are obtained even for very large systems can be rationalized as follows. A necessary requirement for the integral $(\mu\lambda|\nu\sigma)$ to be significant is that basis functions μ and λ show significant overlap (the same holds for ν and σ). This integral will be contracted with the following four density matrix elements: $P_{\mu\nu}$, $P_{\mu\sigma}$, $P_{\lambda\nu}$, and $P_{\lambda\sigma}$. Due to the overlap argument this means that if, for example, $P_{\mu\nu}$ is significant for the contraction with $(\mu\lambda|\nu\sigma)$, then it is very likely (but not guaranteed) that the other three exchange contributions that arise from this integral are too, because they involve density-matrix index pairs that originate from the same spatial regions.

If the same integral codes are employed, then given the

observed permutational factors, the loss of permutational symmetry in ONX¹⁸ means that its crossover relative to employing a conventional SCF code for exact exchange-only is for systems large enough that quadratic screening completely dominates two-electron integral evaluation. For example, if the permutational factor is 3, then conventional screening must be roughly twice as expensive as integral formation and contraction with densities for ONX to break even. Our LinK method is designed to overcome this problem, and provides the best possible performance within the framework of reusing existing integral code. This objective is somewhat complementary to ONX, which via its special loop structure, seems quite well suited to extensions in which the integral code is customized for exchange to yield further speed-ups, which if large enough (greater than the permutational factor itself), could make the loss of the permutational factor worthwhile. Indeed, such ideas offer as well the best chance for further improvements within the LinK framework or even quadratic exchange screening.

IV. CONCLUSION

We have introduced a new scheme (LinK) for the formation of exact (Hartree–Fock-type) exchange matrices, which is capable of achieving linear-scaling of computational effort with molecular size. Our method preserves the highly optimized integral-driven structure of conventional SCF and permits linear scaling by using efficient density-weighted integral screening schemes. We have demonstrated significant speed-ups relative to using conventional direct SCF code to evaluate exact exchange matrices, although quite large molecules are required before the gain by the linear scaling screening scheme is pronounced (since conventional quadratic exchange-only screening becomes dominant only for large systems, if done efficiently). For the exchange-like contractions of density-matrix derivatives with two-electron integrals, as needed in the rate-determining step of the D-CPSCF equations,⁶ we demonstrate that large speed-ups are obtained for significantly smaller system sizes. In such cases computational effort becomes asymptotically independent of system size.

Other applications of the LinK method can be readily imagined, and should be explored in the future. For example, it can be employed to reduce the computational effort and scaling properties of exchange contributions in direct formulations of single excitation configuration interaction and the random phase approximation for excited states (see for example Refs. 25–27 and references therein). Exchangelike contractions also arise in some forms of local electron correlation theory. Finally, we are working on an extension of LinK to the gradient of the exchange energy, which we plan to report on shortly.²⁸

ACKNOWLEDGMENTS

This work is dedicated to the memory of Priv. Doz. Dr. Marco Häser. The authors thank Dr. Matt Challacombe and Eric Schwegler for discussions and for the coordinate files of the water clusters. C.O. acknowledges financial support by a postdoctoral fellowship from the DFG (“Deutsche Forschungsgemeinschaft”). M.H.-G. acknowledges support by

the National Science Foundation (Grant No. CHE-9357129) and by fellowships from the David and Lucile Packard Foundation and the Alfred P. Sloan Foundation.

- ¹J. Almlöf, K. Faegri, Jr., and K. Korsell, *J. Comput. Chem.* **3**, 385 (1982).
- ²D. Cremer and J. Gauss, *J. Comput. Chem.* **7**, 274 (1986).
- ³M. Häser and R. Ahlrichs, *J. Comput. Chem.* **10**, 104 (1989).
- ⁴X.-P. Li, R. W. Nunes, and D. Vanderbilt, *Phys. Rev. B* **47**, 10891 (1993).
- ⁵J. M. Millam and G. E. Scuseria, *J. Chem. Phys.* **106**, 5569 (1997).
- ⁶C. Ochsenfeld and M. Head-Gordon, *Chem. Phys. Lett.* **270**, 399 (1997).
- ⁷C. A. White and M. Head-Gordon, *Chem. Phys. Lett.* **230**, 8 (1994).
- ⁸C. A. White, B. G. Johnson, P. M. W. Gill, and M. Head-Gordon, *Chem. Phys. Lett.* **253**, 268 (1996), and references therein.
- ⁹C. A. White and M. Head-Gordon, *J. Chem. Phys.* **105**, 5061 (1996).
- ¹⁰M. C. Strain, G. E. Scuseria, and M. J. Frisch, *Science* **271**, 51 (1996).
- ¹¹M. Challacombe, E. Schwegler, and J. Almlöf, *J. Chem. Phys.* **104**, 4685 (1996).
- ¹²M. Challacombe and E. Schwegler, *J. Chem. Phys.* **106**, 5526 (1997).
- ¹³B. G. Johnson, C. A. White, Q. Zhang, B. Chen, R. L. Graham, P. M. W. Gill, and M. Head-Gordon, in *Recent Developments in Density Functional Theory*, edited by J. M. Seminario (Elsevier Science, Amsterdam, 1996), Vol. 4, p. 441.
- ¹⁴R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, *Chem. Phys. Lett.* **257**, 213 (1996).
- ¹⁵A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ¹⁶E. Schwegler and M. Challacombe, *J. Chem. Phys.* **105**, 2726 (1996).
- ¹⁷J. C. Burant, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **105**, 8969 (1996).
- ¹⁸E. Schwegler, M. Challacombe, and M. Head-Gordon, *J. Chem. Phys.* **106**, 9708 (1997).
- ¹⁹C. A. White and M. Head-Gordon, *J. Chem. Phys.* **104**, 2620 (1996).
- ²⁰P. Pulay, *J. Chem. Phys.* **78**, 5043 (1983).
- ²¹Y. Osamura, Y. Yamaguchi, P. Saxe, D. J. Fox, M. A. Vincent, and H. F. Schaefer, *J. Mol. Struct.* **103**, 183 (1983).
- ²²M. Frisch, M. Head-Gordon, and J. Pople, *Chem. Phys.* **141**, 189 (1990).
- ²³B. G. Johnson, P. M. W. Gill, M. Head-Gordon, C. A. White, J. Baker, D. R. Maurice, M. Challacombe, E. Schwegler, T. R. Adams, J. Kong, M. Oumi, C. Ochsenfeld, N. Ishikawa, R. D. Adamson, J. P. Dombroski, R. L. Graham, and E. D. Fleischmann, Q-CHEM, Q-Chem Inc., Pittsburgh, PA, 1997, development version.
- ²⁴Coordinates available upon request.
- ²⁵J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, *J. Phys. Chem.* **96**, 135 (1992).
- ²⁶H. Weiss, R. Ahlrichs, and M. Häser, *J. Chem. Phys.* **99**, 1262 (1993).
- ²⁷C. Ochsenfeld, J. Gauss, and R. Ahlrichs, *J. Chem. Phys.* **103**, 7401 (1995).
- ²⁸C. Ochsenfeld, C. A. White, and M. Head-Gordon (in preparation).