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Multiresolution quantum chemistry in multiwavelet bases: Hartree–Fock exchange

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In a previous study [R. J. Harrison *et al.*, J. Chem. Phys. (in press)] we reported an efficient, accurate multiresolution solver for the Kohn–Sham self-consisitent field (KS-SCF) method for general polyatomic molecules. This study presents an efficient numerical algorithm to evalute Hartree–Fock (HF) exchange in the multiresolution SCF method to solve the HF equations. The algorithm employs fast integral convolution with the Poission kernel in the nonstandard form, screening the sparse multiwavelet representation to compute results of the integral operator only where required by the nonlocal exchange operator. Localized molecular obitals are used to attain near linear scaling. Results for atoms and molecules demonstrate reliable precision and speed. Calculations for small water clusters demonstrate a total cost to compute the HF exchange potential for all n_{occ} occpuied MOs scaling as $O(n_{\text{occ}}^{1.5})$. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1790931]

I. INTRODUCTION

In a previous work,[1] we presented a practical multiresolution method[2,3] in multiwavelet bases to solve the all-electron local density approximation (LDA) Kohn–Sham (KS) (Ref. 4) equation for molecules. The approach described in Ref. 5 was employed for the solution of the integral form of the density functional equations. In this paper, we extend the approach to include Hartree–Fock (HF) exchange using an algorithm that will scale asympotically linearly with the molecule size while maintaining a guarantee of arbitrary finite precision.

The evaluation of HF exchange is necessary to determine the electronic wave functions for HF method [6] and the KS method with hybrid exchange functionals (such as B3LYP) (Refs. 7 and 8) as well as post-HF methods. The HF (or exact) exchange term is a nonlocal operator, and this evaluation has been regarded as a major computational bottleneck for electronic structure calculations.[9] The widely used Gaussian basis implementation with the direct self-consistent field (SCF) method[10] demands $O(N^{3-4})$ scaling cost for small and moderate-size molecules, and possibly $O(N^2 \ln N)$ for large systems.[11] Several algorithms have been proposed for $O(N)$ Hartree–Fock exchange in the Gaussian bases,[12–14] based upon assuming or forcing an exponential asymptotic behavior in the density matrix, $\rho(r,r')$ $\sim \exp(-|r-r'|/\ell)$ (Ref. 15), where ℓ is a system-specific length-scale parameter. However, the demonstrations of linear scaling behavior are limited to using relatively small and nondiffuse basis sets for large systems. Diffuse functions are often chemically essential even in HF or density functional theory (DFT) calculations, and present a significant computational challenge in large systems, such as the DNA stacking problem.[16] Furthermore, linear scaling algorithms based upon forcing sparsity unavoidably introduce an error in the total energy that grows with the system size unless the truncation threshold is reduced with the system size. This is not practical for computing small chemical energy differences in very large systems.

These previous methods have relied exclusively upon spatially localized representations to achieve efficiency by introducing sparsity into the density matrix and/or integrals. However, this approach immediately precludes efficient treatment of either the smoothly varying component of density, or dense blocks of the density matrix such as inevitably occur within atoms or between neighboring atoms. Forcing exponential decay in metallic systems or systems with small highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps, such as graphitic sheets, will generate incorrect results since the density matrix does not decay exponentially. The previous $O(N)$ HF exchange method reverts to an $O(N^2)$ complexity in such systems. No systematic analysis has been performed to date on the errors introduced by these exchange approximations. This is an especial concern in multicomponent systems such as required in the study of catalytic processes involving conjugated hydrocarbons on the surface of nanoscale metal particles absorbed on oxide surfaces. In contrast, a multiresolution approach, by separating the behavior of functions between length scales is efficient and maintains a guarantee of precision regardless of the physical composition of the system.

Recent success with hybrid DFT exchange-correlation functionals[7,8] has motivated the development of efficient techniques to include HF exchange in plane-wave (PW) DFT molecular dynamics.[17] A straightforwardly optimized procedure, which was reported by Chawla and Voth[18] in conjunction with the all-electron "projector augmented wave" method,[19] formally scales in $O(n_{\text{occ}}^2 N_{\text{PW}} \ln N_{\text{PW}})$ for both en-

ergy and its gradient (with respect to orbitals) of the HF exchange, where n_{occ} and N_{PW} are the numbers of occupied MOs and plane waves, respectively.

A systematic approach to multiresolution constructions started with the development of wavelet bases, see Ref. 2 and references therein. For numerical applications, the results in Ref. 3 pointed out a practical approach to reducing the computational cost. One of the results of Ref. 3 was the introduction of the nonstandard form (NS-form) for representing operators in multiresolution bases. However, the straightforward generalization of NS-form (or for that matter, the standard form) to multiple dimensions is too expensive for practical applications. Our approach is based on using NS-form and the separated representations of operators that were first used in Ref. 20 and significantly extended in Ref. 21. The basic point of Ref. 21 is that many apparently nonseparable operators are, in fact, separable with a finite but arbitrary precision. Moreover, the number of terms necessary for such representations is remarkably small.

In the following, we first present essential aspect of the numerical approach, describe the algorithm for the HF exchange, then the combination with localized orbitals. Finally, we provide some numerical results and conclusions.

II. MATHEMATICAL BACKGROUND

Multiresolution wavelet and multiwavelet expansions organize functions and operators efficiently in terms of proximity on a given scale and between the length scales.[2,3,5,20] Multiresolution decomposes the Hilbert space $\mathbf{L}^2(\mathbf{R}^d)$, $d \geqslant 1$ into a chain of closed subspaces (refinement scales),

$$\mathbf{V}_0 \subset \mathbf{V}_1 \subset \mathbf{V}_2 \subset \cdots \subset \mathbf{V}_n \subset \cdots . \tag{1}$$

The wavelet subspaces $\mathbf{W}_j$ are defined as an orthogonal complement of $\mathbf{V}_j$ in $\mathbf{V}_{j-1}$, thus

$$\mathbf{V}_n = \mathbf{V}_0 \overset{n}{\underset{j=0}{\oplus}} \mathbf{W}_j . \tag{2}$$

In a previous study,[1] we presented a practical approach for fast computation with integral operators (notably Green functions for the Poisson and bound-state Helmholtz equations) in the NS-form. Let T be an operator such as the integral convolution operator with the kernel K,

$$(T*f)(x) = \int dy \, K(x-y)f(y). \tag{3}$$

As was introduced in Ref. 3, by using orthogonal projection operators $P_j : \mathbf{L}^2(\mathbf{R}^d) \to \mathbf{V}_j$, and $Q_j : \mathbf{L}^2(\mathbf{R}^d) \to \mathbf{W}_j$ with $Q_j = P_{j+1} - P_j$, the NS-form of the operator T is expressed as

$$T_n = T_0 + \sum_{j=0}^{n-1} (A_j + B_j + C_j), \tag{4}$$

where $T_j = P_j T P_j$, $A_j = Q_j T Q_j$, $B_j = Q_j T P_j$, and $C = P_j T Q_j$. This Eq. (4) is derived from a "telescopic" series

$$T_n = (T_n - T_{n-1}) + (T_{n-1} - T_{n-2}) + \cdots + (T_1 - T_0) + T_0 \tag{5}$$

by using $(T_{j+1} - T_j) = A_j + B_j + C_j$. The function $f(x)$ is represented by the projection operators as

$$f_n = P_n f = f_0 + \sum_{j=0}^{n-1} Q_j f. \tag{6}$$

The application of the NS-form of the operator T to the function f, i.e., $T_n f_n$, [Eq. (3)] is also given as a telescopic series

$$T_n f_n = (T_n f_n - T_{n-1} f_{n-1}) + \cdots + (T_1 f_1 - T_0 f_0) + T_0 f_0 . \tag{7}$$

We can rewrite Eq. (7) taking the relation $P_j Q_j = Q_j P_j = 0$ into account,

$$T_n f_n = T_0 f_0 + \sum_{j=0}^{n-1} [A_j(Q_j f) + B_j(P_j f) + C_j(Q_j f)]. \tag{8}$$

In this paper, the elements of T_n are denoted (in one dimension) by

$$[r_{lm}^n]_{ij} = \int dx \, \phi_{il}^n(x) [T \phi_{jm}^n(x)], \tag{9}$$

where $\phi_{il}^n(x)$ is a basis for the projection operator P_n.[5] The elements of A_{n-1}, B_{n-1}, and C_{n-1} (equivalently, $T_n - T_{n-1}$) denoted by α_{lm}^n, β_{lm}^n, and γ_{lm}^n, respectively, are computed from those of T_n by the two-scale relations. The key in NS-form is that this representation of an operator uses bases with supports on squares and has an advantage that it acts scale by scale, without explicitly involving the interactions between different length scales. Futhermore, the sparsity in the multiwavelet space (W_j), which is guaranteed by the vanishing moment property, eventually enables a linear scaling operation as $O[(-\ln \epsilon)N]$, where ϵ is the scheduled accuracy, and N is the number of boxes, or coefficients.

In one dimension the implementation of the above formulation using the kth Legendre polynomial bases is very straightforward for the application of an integral operator with $O[(-\ln \epsilon)k^2 N]$ operation cost. However, in three dimensions the cost is nominally $O[(-\ln \epsilon)k^6 N]$ operations, which has a prohibitively large overhead for a practical code. Separated representations of integral operators[1,20] and use of the low operator rank of the resulting one-dimensional operators, reduce the computational cost to $O[(-\ln \epsilon)k^3 N]$ operations, which enables practical computation with multiwavelet bases in three and higher dimensions.

III. ALGORITHM

Initially, most of the equations are written for simplicity as if in one dimension. The extension to three dimensions is discussed at the end. The application of the Hartree–Fock operator ($\hat{K}$) to a function $[f(x)]$ is given by

$$\hat{K}f(x) = \int dx' \frac{\rho(x,x')}{|x-x'|} f(x'), \tag{10}$$

where the density matrix in coordinate presentation is given by

$$\rho(x,x') = \sum_{\mu}^{n_{occ}} \chi_\mu(x) \chi_\mu^\dagger(x'), \tag{11}$$

where $\chi_\mu(x)$ is the μth occupied molecular orbital (MO), and n_{occ} is the number of occupied MOs.

We already have a fast algorithm in multiwavelet bases to apply Coulomb operator (i.e., the Green's function to the Poisson equation) (Ref. 1), which may be used to implement exchange in a straightforward fashion, as follows:

$$\hat{K}f(x)=\sum_{\mu}^{n_{\text{occ}}} \chi_{\mu}(x) \int dx' \frac{\chi_{\mu}^{\dagger}(x')f(x')}{|x-x'|}.$$ (12)

This is evaluated by looping over MOs (χ_{μ}), and forming the product of the MO with the target function (f); applying the Coulomb operator; and multiplying the resulting potential by the MO.

During each iteration of the solution of the Hartree–Fock equations, this operator must be applied to each occupied orbital. Therefore, the nominal cost of this approach is roughly $O(Vn_{\text{occ}}^2)$, where V is the system volume. The dependence on V will probably be weaker than this due to the adaptive multiresolution representation and the potential being smooth at long range. Therefore V might be neglected from scaling expressions hereafter. If the occupied orbitals are localized (or, equivalently, if the density matrix is sparse), there will only be $O(n_{\text{occ}})$ nonzero products of the occupied orbitals, and the above algorithm reduces to $O(Vn_{\text{occ}})$. The factor proportional to the system volume arises from computing in all space the electrostatic potential due to the product $\chi(x')f(x')$. However, the very next step in the algorithm is multiplication by the localized MO. If the algorithm that applies the Coulomb operator is modified to compute the potential only in the volume where the MO is significant, the overall cost can be reduced to $O(n_{\text{occ}})$, or $O(1)$ for each localized target function.

Our goal is to modify the Coulomb operator so that it computes the potential to the required precision in the volume where the localized MO is significant, and outside this volume does as little work as possible. Since the NS-form[3] of the Coulomb operator computes contributions at all length scales, it is inevitable that there will be nonzero values outside of the desired minimum volume. However, the finer-scale contributions need to be computed only where necessary, and only to a precision controlled, in part, by the magnitude of the orbital.

We denote the product of a MO [$\chi(x)$] and the target function [$f(x)$] by $g(x)=\chi(x)f(x)$, and the electrostatic potential due to the charge density $g(x)$ by $u(x)$. Then in some subvolume Ω we wish to determine if the exchange potential may be neglected. A norm-wise bound on the contribution may be obtained from the Schwarz inequality

$$\left| \int_{\Omega} \chi(x)u(x)dx \right| \leqslant \left(\int_{\Omega} \chi^2(x)dx \right)^{1/2} \left(\int_{\Omega} u^2(x)dx \right)^{1/2}.$$ (13)

The 2-norm of a function in the scaling function basis is simply the 2-norm of the coefficients, since the basis functions are orthonormal.

The potential is formed from the product of the matrix representation at level n of the Coulomb operator (T^n with elements $[r_{lm}^n]_{ij}$) and the function coefficients (g_{li}^n)

$$u_{li}^n = \sum_{mj} [r_{lm}^n]_{ij} g_{mj}^n.$$ (14)

The translation l labels a subvolume at level n. Due to the multiscale summation, and also to minimize the computation, we must screen each contribution separately. A norm-wise bound for contribution in box l from box m is provided by the Schwarz inequality, which for matrices becomes the Frobenius norm

$$\|r_{lm}^n g_m^n\|_F \leqslant \|r_{lm}^n\|_F \|g_m^n\|_F.$$ (15)

At each level of the multiscale summation, the dominant contributions come from the box and its 26 nearest neighbors, so we can neglect contributions if

$$\|s_l^n\|_F \|r_{lm}^n\|_F \|g_m^n\|_F \leqslant \frac{\epsilon}{27 n_{\text{max}}}.$$ (16)

The multiscale summation over the n_{max} refinement levels is accomplished through the nonstandard form [Eq. (5)]. The difference $T_n - T_{n-1}$ decays very rapidly with distance since the long range (i.e., smoother) parts of the operator are accurately represented at the coarser levels. Thus, the screening is in practice performed using

$$\|s_l^n\|_2 \|r_{lm}^n - r_{lm}^{n-1}\|_2 \|g_m^n\|_2 \leqslant \frac{\epsilon}{27 n_{\text{max}}}.$$ (17)

The norm of the target function [$g(x)=\chi_{\mu}(x)f(x)$] in each box can be precomputed and stored. Since the Coulomb operator is an integral convolution, the matrix r_{lm}^n actually only depends upon $l-m$. Furthermore, the operator is homogeneous and, therefore, the matrix at level n can be obtained by rescaling the matrix at level 0. These properties permit the operator matrices to be computed as needed with little computational overhead. Finally, the norm of the molecular orbital in each box in which it is significant can also be precomputed and stored. During the application of the operator, the norm of the MO may be required in a box which has not been precomputed. This can happen during the computation of contributions at a locally finer or coarser level than that required to resolve the MO. In this instance, the two-scale relationship[5,22] can be used to compute the missing coefficients. This additional computational cost is minimized by appropriate ordering of the screening tests and loops, and by reuse in the application of the exchange operator to multiple target functions.

The algorithm that applies the screened Coulomb operator to $g(x)$ is then as follows:

```
loop over levels n
    loop over translations (1-m) sorted by magnitude and shell
        Compute T[0][1-m] at level 0 or rescale to get T[n][1-m]
        Recur T[n-1][(1-m)/2] down to level n
        Form the non-standard form operator NS=(T[n]-T[n-1])
        loop over non-zero translations m in g[n]
            l=(1-m)+m
            if |NS|*|g[n][m]|>eps/(27*nmax)
                if |NS|*|g[n][m]|*|s[n][1]|>eps/(27*nmax)
                    u[n][1]=u[n][1]+NS*g[n][m]
                end if
            end if
        end loop
        if no contributions were significant
            go to next n
        end if
    end loop
end loop
```

Since the multiwavelets have at least k vanishing moments (or multipoles), the numerical significance of the coefficient block α_{lm}^n, which is one of NS-form elements (denoted by "$|NS|$" in the above algorithm) of the interaction with the kernel of Poisson equation ($|r-r'|^{-1}$) in full multiwavelet representation, will be asymptotically proportional to $|l-m|^{-2k-1}$. Also, the most slowly decaying elements in the other two blocks of NS-form elements, β_{lm}^n, and γ_{lm}^n, decays as $|l-m|^{-k-1}$. Furthermore, the multiscale representation of the function will introduce additional sparsity. Since we usually use Legendre polynomials of relatively high order ($k=5,7,9$) for reliable calculations, each submatrix of the operator in NS-form is expected to be significant just in a narrow band around the diagonal. This aspect leads to the linear-scaling computation cost in the application of the operator to the function.

The extension to three dimension is accomplished by replacing the translations (l and m) and the multiwavelet indices (i and j) with three vectors. However, as previously described in Ref. 1, an efficient algorithm requires the use of a separated form for the operator to reduce the effective scaling to quartic in order of the multiwavelet. The separated form is given by

$$[r^n_{l_x l_y l_z l'_x l'_y l'_z}]_{stus't'u'} = \sum_\nu [X^{n(\nu)}_{l_x l'_x}]_{ss'}[Y^{n(\nu)}_{l_y l'_y}]_{tt'}[Z^{n(\nu)}_{l_z l'_z}]_{uu'},$$

(18)

and the number of terms included in the summation over μ is referred to as the separation rank of the operator in analogy to the two-dimensional singular-value decomposition. A suboptimal separation is currently obtained by fitting $1/r$ (the kernel of the Coulomb operator) to a sum of Gaussian over a large range of r. The matrix elements of the one-dimensional operators (Gaussian convolutions) are readily generated as described in Refs. 1, 3, and 5.

Application of the separated nonstandard form ($T^n_{lm} - T^{n-1}_{lm}$) of the operator can be accomplished in several ways. The most straightforward is to apply separately T^n_{lm}

and T^{n-1}_{lm}, and then to subtract the results. However, this is both inefficient and can result in loss of significant digits. A better approach is subtract the separated representations of the two operators and then perform a rank reduction as described in Ref. 21. The NS operator is expected to be low rank,[21] and, it is possible to avoid some of the loss of precision. The most accurate, and potentially most efficient, approach is to use the two-scale relationship to form individually the 63 blocks of the nonstandard form,[3,5] each in a separated representation. This avoids the loss of precision arising from taking the difference $T^n_{lm} - T^{n-1}_{lm}$ and permits exploitation of the differing sparsity in each block of the nonstandard form. However, in the separated representation the necessary code is much more complicated and we have not yet pursued this approach.

IV. LOCALIZATION OF ORBITALS

Our formulation for the HF method is based on the canonical molecular orbitals (CMOs) [i.e., $\chi_\mu = -2\hat{G} * (V \cdot \chi_\mu)$], which are spatially delocalized. In our implementation of the integral operators, the Coulomb potential can be computed in $O(Vn_{occ})$ due to the locality of the density function $\rho(x)$, which is invariant to the unitary transformation among the occupied MOs, whereas the computational cost to apply the HF exchange operator to all of the occupied MOs depends on the spatiality of the MOs. The nominal cost of the HF exchange operator with all of the delocalized CMOs is estimated to be roughly $O(Vn_{occ}^2)$. The quadratic dependence on n_{occ} can be reduced by using the localized molecular orbitals (LMOs) via the cutoff mechanism implemented in NS-form of the HF exchange operator. The LMOs are obtained via the unitary transformation among the CMOs as

$$\chi_i^{LMO} = \sum_j^{n_{occ}} U_{ij} \chi_j^{CMO},$$

(19)

where U is an unitary matrix giving a rotation between the CMOs and LMOs. The HF exchange operator to all of CMOs is calculated via the unitary transformation of HF exchange for all of the LMOs as

$$\hat{K}^{\text{CMO}}\chi_i^{\text{CMO}}(x)$$

$$=\sum_{\mu}^{n_{\text{occ}}} \chi_{\mu}^{\text{CMO}}(x)\int dx' \frac{\chi_{\mu}^{\text{CMO}\dagger}(x')\chi_i^{\text{CMO}}(x')}{|x-x'|},$$

$$=\sum_{j}^{n_{\text{occ}}} U_{ji}^* \sum_{\mu}^{n_{\text{occ}}} \chi_{\mu}^{\text{LMO}}(x)\int dx' \frac{\chi_{\mu}^{\text{LMO}\dagger}(x')\chi_j^{\text{LMO}}(x')}{|x-x'|}, \quad (20)$$

$$=\sum_{j}^{n_{\text{occ}}} U_{ji}^*[\hat{K}^{\text{LMO}}\chi_j^{\text{LMO}}(x)].$$

The algorithm to compute HF exchange via LMOs is summarized as follows:

(1) Obtain the unitary matrix for Foster-Boys localization.[23] The matrix is simply obtained from the $n_{\text{occ}} \times n_{\text{occ}}$ matrix of one-electron dipole integrals $\langle\chi_{\mu}^{\text{CMO}}|\mathbf{r}|\chi_{\nu}^{\text{CMO}}\rangle$, which are efficiently computed as inner products.

(2) Apply the rotation and store the LMOs, χ_j^{LMO}, $j = 1,...,n_{\text{occ}}$ [Eq. (19)].

(3) Apply the HF exchange operator to all of the LMOs, $\hat{K}^{\text{LMO}}\chi_j^{\text{LMO}}(x)$, $j = 1,...,n_{\text{occ}}$.

(4) Transform back to the CMOs basis by the unitary matrix [Eq. (20)].

V. RESULTS

A. Hartree−Fock calculation on atoms

An initial test of the implementation was performed upon the neutral atoms He, Be, Ne, Mg, Ca, and Sr. Table I lists the total and the HOMO energies along with the results of Thakkar and co-workers.[24] In the multiresolution calculations, the nuclear potential smoothing parameter was chosen so as to yield an energy accurate to at least 10^{-6} hartree (denoted by $\epsilon_{\text{nuc}} = 10^{-6}$), the box size was set as $L = 80$ bohrs and D_{2h} symmetry was used. We could not use LMOs because the symmetry usage forced the MOs to be delocalized. We used the seventh and ninth order multiwavelet bases and solved to a residual in the MOs [denoted by $r(\text{MO})$] of 10^{-5} and 10^{-6}, respectively. For the Ca and Sr atoms, a more precise calculation with $k = 11$ and $r(\text{MO}) = 10^{-6}$ was additionally carried out. The results agree with the atomic data from Thakkar, which was calculated with Slater-type functions to predict total energies within around 10^{-6} hartree, which is the accuracy delivered in the previous testing LSDA calculations.[1] Systematic convergence to the correct atomic limit is observed in the multiresolution calculations. For all the test atoms except Sr, the ninth order multiwavelet bases reproduce Thakkar's results for the total energies with the five decimals. For Sr, the 11th multiwavelet bases give an excellent agreement with Thakkar's total energy within 1×10^{-6} hartree. The accuracies of the total energies obtained by the seventh multiwavelet bases are 9×10^{-8}, 2×10^{-6}, 2×10^{-5}, 5×10^{-5}, 9×10^{-5}, and 4×10^{-4} hartree for He, Be, Ne, Mg, Ca, and Sr, respectively. For Ca and Sr, the ninth multiwavelet bases yield the accuracy as 3×10^{-6} and 2×10^{-5} hartree for the total energy, respectively.

TABLE I. Total and HOMO energy (in hartree) for atomic Hartree–Fock calculations. $L = 80$ bohrs and $\epsilon_{\text{nuc}} = 10^{-6}$.

Accuracy	Total energy	HOMO energy
	He	
$k=7$, $r(\text{MO}) \leqslant 10^{-5}$	−2.861 680 14	−0.917 955
$k=9$, $r(\text{MO}) \leqslant 10^{-6}$	−2.861 680 23	−0.917 955
Thakkar	−2.861 680 00	−0.917 956
	Be	
$k=7$, $r(\text{MO}) \leqslant 10^{-5}$	−14.573 022	−0.309 267
$k=9$, $r(\text{MO}) \leqslant 10^{-6}$	−14.573 023	−0.309 269
Thakkar	−14.573 023	−0.309 270
	Ca	
$k=7$, $r(\text{MO}) \leqslant 10^{-5}$	−676.758 093	−0.195 529
$k=9$, $r(\text{MO}) \leqslant 10^{-6}$	−676.758 189	−0.195 529
$k=11$, $r(\text{MO}) \leqslant 10^{-6}$	−676.758 186	−0.195 529
Thakkar	−676.758 182	−0.195 530
	Ne	
$k=7$, $r(\text{MO}) \leqslant 10^{-5}$	−128.547 079	−0.850 406
$k=9$, $r(\text{MO}) \leqslant 10^{-6}$	−128.547 098	−0.850 409
Thakkar	−128.547 098	−0.850 410
	Mg	
$k=7$, $r(\text{MO}) \leqslant 10^{-5}$	−199.614 589	−0.253 051
$k=9$, $r(\text{MO}) \leqslant 10^{-6}$	−199.614 637	−0.253 052
Thakkar	−199.614 636	−0.253 052
	Sr	
$k=7$, $r(\text{MO}) \leqslant 10^{-5}$	−3131.545 280	−0.178 455
$k=9$, $r(\text{MO}) \leqslant 10^{-6}$	−3131.545 704	−0.178 456
$k=11$, $r(\text{MO}) \leqslant 10^{-6}$	−3131.545 684	−0.178 456
Thakkar	−3131.545 683	−0.178 453

B. Hartree−Fock calculation on diatomic molecules

Hartree–Fock calculations were performed upon several homonuclear/heteronuclear diatomic molecules near their equilibrium geometries. The molecules and their bond lengths are from a previous study by Pahl and Handy.[25] For the mononuclear diatomic molecules, we computed H_2, C_2, N_2, and F_2 with the bond lengths 1.400, 2.358, 2.068, and 2.668 bohrs, respectively. For the heteronuclear systems BH, HF, BF, CO, and NO^+ with the bond lengths 2.3289, 1.7328, 2.386, 2.132, and 2.0092 bohrs. The box size was set as the bond length times 32 bohrs in order to locate the nuclei at dyadic points.

Tables II and III list the total and HOMO energies for the diatomic molecules, and the dipole moments for the heteronuclear molecules. The results for the homonuclear diatomic molecules were obtained with the D_{2h} symmetry and with the nuclear potentials smoothed within the accuracy 10^{-6} and 10^{-7} hartree (denoted by $\epsilon_{\text{nuc}} = 10^{-6}$ and 10^{-7}, respectively). For the heteronuclear diatomic molecules, we used C_{2v} symmetry and $\epsilon_{\text{nuc}} = 10^{-6}$. The tables include the extrapolated results reported by Pahl and Handy,[25] the numerical Refs. 26 and 27, and the Gaussian calculations with aug-cc-pVXZ, ($X = T, Q, 5$) (Ref. 28) using the NWCHEM program package.[29]

As to the homonuclear diatomic molecules, the most accurate multiresolution results obtained were with 11th multiwavelet bases, residuals of MOs $r(\text{MO}) < 10^{-6}$, and $\epsilon = 10^{-7}$. Our calculations show systematic convergence

J. Chem. Phys., Vol. 121, No. 14, 8 October 2004

Multiresolution quantum chemistry 6685

TABLE II. Total and HOMO energy (in hartree) for Hartree–Fock calculations for homonuclear diatomic molecules.

Accuracy	Total energy	HOMO energy
H_2 ($L=1.4\times 32$ bohr)		
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-6}$	$-1.133\,629\,77$	$-0.594\,658$
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-7}$	$-1.133\,629\,44$	$-0.594\,658$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-6}$	$-1.133\,629\,81$	$-0.594\,657$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-1.133\,629\,59$	$-0.594\,658$
$k=11$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-1.133\,629\,59$	$-0.594\,658$
PH result (extrapolated)[a]	$-1.133\,629\,55$	$-0.594\,673$
Numerical[b]	$-1.133\,626\,57$	
aug-cc-pVTZ	$-1.133\,026\,85$	$-0.594\,401$
aug-cc-pVQZ	$-1.133\,473\,02$	$-0.594\,616$
aug-cc-pV5Z	$-1.133\,610\,66$	$-0.594\,653$
C_2 ($L=2.358\times 32$ bohr)		
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-6}$	$-75.406\,550$	$-0.456\,802$
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-7}$	$-75.406\,550$	$-0.456\,803$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-6}$	$-75.406\,565$	$-0.456\,802$
$k=9$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-7}$	$-75.406\,565$	$-0.456\,803$
$k=11$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-75.406\,565$	$-0.456\,803$
PH result (extrapolated)[a]	$-75.406\,562$	$-0.456\,777$
Numerical[c]	$-75.406\,565$	
aug-cc-pVTZ	$-75.401\,722$	$-0.456\,741$
aug-cc-pVQZ	$-75.405\,727$	$-0.456\,802$
aug-cc-pV5Z	$-75.406\,438$	$-0.456\,802$
N_2 ($L=2.068\times 32$ bohr)		
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-6}$	$-108.993\,801$	$-0.615\,624$
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-7}$	$-108.993\,802$	$-0.615\,624$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-6}$	$-108.993\,826$	$-0.615\,624$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-108.993\,825$	$-0.615\,624$
$k=11$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-108.993\,825$	$-0.615\,624$
PH result (extrapolated)[a]	$-108.993\,814$	$-0.615\,595$
Numerical[c]	$-108.993\,81$	
aug-cc-pVTZ	$-108.985\,317$	$-0.615\,972$
aug-cc-pVQZ	$-108.992\,205$	$-0.615\,688$
aug-cc-pV5Z	$-108.993\,602$	$-0.615\,634$
F_2 ($L=2.668\times 32$ bohr)		
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-6}$	$-198.773\,423$	$-0.666\,931$
$k=7$, $r(MO)\leqslant 10^{-5}$, $\epsilon_{nuc}=10^{-7}$	$-198.773\,424$	$-0.666\,931$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-6}$	$-198.773\,445$	$-0.666\,931$
$k=9$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-198.773\,445$	$-0.666\,931$
$k=11$, $r(MO)\leqslant 10^{-6}$, $\epsilon_{nuc}=10^{-7}$	$-198.773\,445$	$-0.666\,930$
PH result (extrapolated)[a]	$-198.773\,446$	$-0.666\,921$
Numerical[c]	$-198.773\,323$	
aug-cc-pVTZ	$-198.754\,789$	$-0.667\,496$
aug-cc-pVQZ	$-198.769\,003$	$-0.667\,094$
aug-cc-pV5Z	$-198.773\,009$	$-0.666\,937$

[a]Reference 25.
[b]Reference 26.
[c]Reference 27.

TABLE III. Total and HOMO energy (in hartree) and dipole moment (in debye) for Hartree–Fock calculations for heteronuclear diatomic molecules, $\epsilon=10^{-6}$.

Accuracy	Total energy	HOMO energy	Dipole
BH ($L=2.3289\times 32$ bohrs)			
$k=7$, $r(MO)\leqslant 10^{-5}$	$-25.131\,636$	$-0.348\,325$	1.741 010
$k=9$, $r(MO)\leqslant 10^{-6}$	$-25.131\,639$	$-0.348\,324$	1.741 010
PH result (extrapolated)[a]	$-25.131\,639$	$-0.348\,290$	
Numerical[b]	$-25.131\,639$		
aug-cc-pVTZ	$-25.130\,201$	$-0.348\,138$	1.744 913
aug-cc-pVQZ	$-25.131\,371$	$-0.348\,289$	1.740 969
aug-cc-pV5Z	$-25.131\,597$	$-0.348\,320$	1.741 026
HF ($L=1.7328\times 32$ bohrs)			
$k=7$, $r(MO)\leqslant 10^{-5}$	$-100.070\,776$	$-0.650\,392$	1.921 760
$k=9$, $r(MO)\leqslant 10^{-6}$	$-100.070\,803$	$-0.650\,394$	1.921 760
PH result (extrapolated)[a]	$-100.070\,795$	$-0.650\,380$	
Numerical[b]	$-100.070\,82$		
aug-cc-pVTZ	$-100.061\,071$	$-0.650\,547$	1.925 343
aug-cc-pVQZ	$-100.068\,561$	$-0.650\,454$	1.922 380
aug-cc-pV5Z	$-100.070\,575$	$-0.650\,398$	1.921 949
BF ($L=2.386\times 32$ bohrs)			
$k=7$, $r(MO)\leqslant 10^{-5}$	$-124.168\,761$	$-0.405\,110$	0.871 343
$k=9$, $r(MO)\leqslant 10^{-6}$	$-124.168\,780$	$-0.405\,112$	0.871 334
PH result (extrapolated)[a]	$-124.168\,77$	$-0.405\,087$	
Numerical[b]	$-124.168\,85$		
aug-cc-pVTZ	$-124.157\,207$	$-0.405\,220$	0.872 941
aug-cc-pVQZ	$-124.166\,299$	$-0.405\,127$	0.870 991
aug-cc-pV5Z	$-124.168\,516$	$-0.405\,110$	0.871 333
CO ($L=2.132\times 32$ bohrs)			
$k=7$, $r(MO)\leqslant 10^{-5}$	$-112.790\,878$	$-0.554\,926$	0.264 969
$k=9$, $r(MO)\leqslant 10^{-6}$	$-112.790\,907$	$-0.554\,924$	0.264 975
PH result (extrapolated)[a]	$-112.790\,902$	$-0.554\,880$	
Numerical[b]	$-112.790\,95$		
aug-cc-pVTZ	$-112.781\,447$	$-0.554\,932$	0.266 883
aug-cc-pVQZ	$-112.789\,052$	$-0.554\,919$	0.265 204
aug-cc-pV5Z	$-112.790\,674$	$-0.554\,915$	0.264 908
NO^+ ($L=2.0092\times 32$ bohrs)			
$k=7$, $r(MO)\leqslant 10^{-5}$	$-128.977\,710$	$-1.139\,074$	0.475 307
$k=9$, $r(MO)\leqslant 10^{-6}$	$-128.977\,740$	$-1.139\,079$	0.475 362
PH result (extrapolated)[a]	$-128.977\,727$	$-1.139\,034$	
Numerical[b]	$-128.977\,78$		
aug-cc-pVTZ	$-128.966\,245$	$-1.139\,008$	0.473 470
aug-cc-pVQZ	$-128.975\,514$	$-1.139\,006$	0.475 197
aug-cc-pV5Z	$-128.977\,459$	$-1.139\,075$	0.475 445

[a]Reference 25.
[b]Reference 27.

with an accuracy of at least 10^{-6} hartree for the total energies. We observed that the total energies are already converged with ninth multiwavelet bases and $r(MO)\leqslant 10^{-6}$ within the accuracy 10^{-6} hartree. There is no significant error within an expected accuracy between two smoothing parameters $\epsilon_{nuc}=10^{-6}$ and $\epsilon_{nuc}=10^{-7}$, as expected. The resulting total energies agree with the previous numerical calculations[26,27] (to at least three decimal places) and with those of Pahl and Handy (at least four decimal places). The best total energy of the H_2 molecule we computed,

$-1.133\,629\,593$ ($k=11$), is satisfactorily accurate with comparison to the most accurate value in the literature, $-1.113\,629\,5717$ (Ref. 26). For the F_2 molecule we found an apparent error of 1.2×10^{-4} hartree in the previous numerical result.[27] The deviations of aug-cc-pV5Z from the multiresolution calculations with the 11th multiwavelet bases are 1.9×10^{-5}, 1.2×10^{-4}, 2.2×10^{-4}, and 4.4×10^{-4} hartree for the total energies of H_2, C_2, N_2, and F_2, respectively.

Since we observed that the ninth order multiwavelet bases $r(MO)\leqslant 10^{-6}$ and $\epsilon_{nuc}=10^{-6}$ gave sufficient accuracy, we did not use either the 11th multiwavelet bases or $\epsilon_{nuc}=10^{-7}$ for the hetronuclear diatomic molecules. For these molecules, the dipole moments were also computed, the implementation of which is discussed elsewhere.[30] The

TABLE IV. Total and HOMO energy (in hartree) and CPU timings (in sec) for Hartree–Fock calculations for benzene molecule, $\epsilon_{nuc} = 10^{-6}$.

Accuracy	Total energy (in hartree)	HOMO energy (in hartree)	Timing: Coulomb (sec)	Timing: HF exchange (sec)	Timing: Localization (sec)	No. of blocks each MOs (CMO/LMO)
			$k=7, r(MO) \leqslant 3 \times 10^{-4}$			
D_{2h}	−230.798 692	−0.337 991	8.7	699 (33)		61/–
C_1 with CMOs for HF exch.	−230.798 479	−0.338 012	80	6155 (293)		457/–
C_1 with LMOs for HF exch.	−230.798 612	−0.337 994	ditto	3060 (146)	152	495/376
			$k=9, r(MO) \leqslant 3 \times 10^{-4}$			
D_{2h}	−230.798 768	−0.338 058	110	9770 (465)		259/–
C_1 with CMOs for HF exch.	−230.798 768	−0.338 040	860	81 200 (3870)		2125/–
C_1 with LMOs for HF exch.	−230.798 768	−0.338 068	ditto	30 400 (1450)	1110	2170/1064
PH result (extraploated)	−230.798 7	−0.338 025				
aug-cc-pVTZ	−230.782 244	−0.337 984				
aug-cc-pVQZ	−230.795 403	−0.338 044				
aug-cc-pV5Z	−230.798 272	−0.338 050				

results for the total energy again agree to three decimal places with the previous numerical calculations[27] and to four places with those of Pahl and Handy.[25] The differences in the energy between the multiresolution calculations with the 9th multiwavelet bases and aug-cc-pV5Z are 4.2×10^{-5}, 2.3×10^{-4}, 2.6×10^{-4}, 2.3×10^{-4}, and 2.7×10^{-4} hartree for the total energies of BH, HF, BF, CO, and NO$^+$, respectively. The maximum difference in dipole moments is 1.9×10^{-4} debye for HF molecule.

C. Hartree–Fock calculation for the benzene molecule

HF calculations were performed upon the benzene molecule. We took the same geometry, $R_{C-C} = 1.3862$ Å and $R_{C-H} = 1.0756$ Å, as used by Pahl and Handy.[25,31] The nuclear potentials were smoothed with $\epsilon_{nuc} = 10^{-6}$, and the box size was set to $L = 45$ bohrs. We used the seventh and ninth order multiwavelet bases with $r(MO) \leqslant 3 \times 10^{-4}$. The calculations were performed using both D_{2h} and C_1 symmetry. In the C_1 symmetry, we employed both the CMOs and also the LMOs to verify the accuracy and efficiency of the LMOs-based HF exchange method. In summary, three calculations were performed: with D_{2h} symmetry, without symmetry in CMOs, and without symmetry in LMOs. Table IV shows the total and HOMO energies, the timings for applying HF exchange operators and the localization to all of the MOs, and the number of coefficient blocks for the multiwavelet bases (their Frobenius norm $> 5 \times 10^{-k}$) for each CMO/LMO. The parentheses in the timing columns mean the average times for each MO. The central processing unit (CPU) time was measured on a single 1.3 GHz Power4 processor on IBM p690 system.

The ninth order multiwavelet bases with $r(MO) \leqslant 3 \times 10^{-4}$ yielded consistent results for the three calculations. For the seventh order multiwavelet bases, the differences in the total energies are within 1×10^{-4} hartree. The deviation of the total energies with the seventh order multiwavelet bases from the ninth order multiwavelet bases is $1-2 \times 10^{-4}$ hartree. Pahl and Handy's result agrees with the mul-

tiresolution calculation within the available digits. The aug-cc-pV5Z basis has an error of 5×10^{-4} hartree in the total energy.

The times for applying the HF exchange operator with the D_{2h} symmetry is around eight times faster than that for the CMO-based HF exchange operator with the C_1 symmetry. The eightfold speed up is an expected computational reduction by the spatial symmetry usage in our implementation. The same scale is also observed in reduction of the number of coefficient blocks between D_{2h} and C_1 calculations. By using LMOs, the timing are improved by factors of 1.9 and 2.6 for the seventh and ninth multiwavelet bases, respectively. The times for the localization were negligibly small, around 3% of total times for applying the HF exchange operator. The localization reduces the numbers of blocks to 76% and 49% for the seventh and ninth order multiwavelet bases, respectively.

D. Computational scaling of Hartree–Fock exchange for $n[H_2O]$, $n=1, 2, 3$

We examined the computational scaling of the Hartree–Fock exchange calculation using the water monomer, dimer, and trimer, whose geometries are listed in Table V. Table VI shows the total and HOMO energies, the timings to compute HF exchange and localize MOs, the numbers of coefficient

TABLE V. The geometries (in bohr) for $n[H_2O]$, $n=1, 2, 3$.

	x	y	z
		Water 1	
O	0.0	0.0	0.0
H	±1.4375	0.0	1.15
		Water 2	
O	4.0	0.0	5.0
H	4.0±1.4375	0.0	5.0+1.15
		Water 3	
O	−4.0	0.0	−5.0
H	−4.0±1.4375	0.0	−5.0+1.15

[a] $r(O-O) = 6.4$ bohr $= 3.4$ Å.

TABLE VI. Total and HOMO energy (in hartree) and CPU timings (in sec) for Hartree–Fock calculations for $n[H_2O]$, $n = 1, 2, 3$, $\epsilon_{nuc} = 10^{-6}$.

Accuracy	Total energy (hartree)	HOMO energy (hartree)	Timing: Coulomb (sec)	Ratio	Timing: HF exchange (sec)	Timing: Localization (sec)	Ratio	No. of blocks each MOs (CMO/LMO)
			$k=7$, $r(MO) \leqslant 3 \times 10^{-4}$					
Monomer ($n=1$)								
CMOs for HF exchange	−76.065 573	−0.509 731	22	1.0	243 (48)		1.00 (1.00)	222/–
LMOs for HF exchange	−76.065 575	−0.509 743	ditto		198 (40)	9	0.81 (0.81)	202/199
Dimer ($n=2$)								
CMOs for HF exchange	−152.134 176	−0.493 340	43	2.0	889 (89)		3.66 (1.83)	274/–
LMOs for HF exchange	−152.134 218	−0.493 038	ditto		516 (52)	27	2.12 (1.06)	248/228
Trimer ($n=3$)								
CMOs for HF exchange	−228.203 507	−0.488 169	70	3.2	1620 (107)		6.67 (2.22)	313/–
LMOs for HF exchange	−228.203 526	−0.487 890	ditto		1090 (73)	55	4.49 (1.50)	291/237
			$k=9$, $r(MO) \leqslant 3 \times 10^{-4}$					
Monomer ($n=1$)								
CMOs for HF exchange	−76.065 596	−0.509 721	235	1.0	2220 (444)		1.00 (1.00)	817/–
LMOs for HF exchange	−76.065 595	−0.509 748	ditto		1930 (386)	60	0.87 (0.87)	848/719
Dimer ($n=2$)								
CMOs for HF exchange	−152.134 260	−0.493 355	445	2.0	8390 (839)		3.78 (1.89)	964/–
LMOs for HF exchange	−152.134 261	−0.493 178	ditto		5320 (532)	166	2.40 (1.20)	955/766
Trimer ($n=3$)								
CMOs for HF exchange	−228.203 614	−0.488 041	690	3.1	18 100 (1200)		8.15 (2.72)	1297/–
LMOs for HF exchange	−228.203 614	−0.487 975	ditto		9815 (654)	346	4.42 (1.47)	1123/832
aug-cc-pVQZ				Fock building and diagonalization				
Monomer ($n=1$)	−76.064 329	−0.509 631			75		1.0	
Dimer ($n=2$)	−152.131 759	−0.493 169			940		12.5	
Trimer ($n=3$)	−228.199 857	−0.487 951			3000		40.0	

blocks (their Frobenius norm $> 5 \times 10^{-k}$). The parentheses in the timing columns mean the averages for each MO. The table also includes the CPU times for computing Coulomb potential. The calculations were performed with the C_1 symmetry, $\epsilon_{nuc} = 10^{-6}$, and the box size $L = 60$ bohr. The seventh and ninth order multiwavelet bases were used with $r(MO) \leqslant 3 \times 10^{-4}$. The results were obtained in two approaches to compute the HF exchange using CMOs and LMOs, so that we can directly compare the computational scaling between the two approaches. Table VI includes the ratios of timings against the CMO-based HF exchange calculation for the monomer. The same calculations were carried out using NWCHEM with the default screening threshold.

As to the accuracy, the calculations with the CMO- and LMO-based HF exchange in the ninth order multiwavelet bases yield total energies consistent within 10^{-6} hartree, and those in the seventh order multiwavelet bases agreed with those in ninth order multiwavelet bases at the first six digits.

Overall, the LMOs reduce the computational demanding for applying the HF exchange operator. Even for the monomer, the CPU time for LMOs was 10%–15% faster than that for CMOs. The timing ratios for the total operation for all MOs are estimated as $1.0 \times n^{1.74}$ ($k=7$, CMOs), $0.79 \times n^{1.53}$ ($k=7$, LMOs), $1.0 \times n^{1.91}$ ($k=9$, CMOs), and $0.87 \times n^{1.48}$ ($k=9$, LMOs). The best scaling for the HF exchange calculation for this system is obtained as 1.5 on the number of waters, which is successfully smaller than quadratic scaling. We note the Coulomb potential is computed in $O(n)$ scaling.

VI. CONCLUSION

An accurate, efficient algorithm has been presented to compute the HF exchange operator using multiresolution analysis in multiwavelet bases. The present implementation of the HF exchange in MADNESS (Ref. 32) is a straightforward extension of the fast algorithm in multiwavelet bases to apply Coulomb operator (i.e., the Green's function to the Poisson equation) in three dimensions. We use the NS-form for application of the operator to the function, which allows us to do the application in a linear scaling fashion and efficiently within a guaranteed finite accuracy. Specifically for the HF exchange operator, we have implemented screening for the weak nonlocal interaction in the HF exchange to avoid $O(n_{occ}^2)$ scaling operation for each target MO or totally $O(n_{occ}^3)$ scaling for all the occupied MOs. The asymptotic scaling is formally reduced to a total operation cost to $O(n_{occ})$, or $O(1)$ for each target localized MO.

We demonstrated the HF SCF calculations for the many-electron closed-shell systems including a number of atoms, diatomic molecules, polyatomic molecules such as benzene molecule and water monomer, dimer and trimer. The performance was satisfactory in that the results yielded the required precision, and the computational cost was observed to scale as expected.

We used Foster-Boys's LMOs for the HF exchange calculations to enhance the sparsity. The illustrative calculations using benzene and water trimer demonstrated that the LMOs worked efficiently to reduce the computational cost and scal-

ing in the C_1 symmetry without losing accuracy. In the water cluster, we observed a computational scaling for LMO-based HF exchange of $O(n_{occ}^{0.5})$ for each target MO, and $O(n_{occ}^{1.5})$ for all the occupied MOs.

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