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)

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:

$\epsilon\phi$ $\epsilon\phi\hat{K}\phi\alpha$ $\Sigma\epsilon\Sigma\phi\alpha$ Σ Σ $\epsilon\phi$ $\phi\alpha$

```
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]
         1=(1−m)+m
         if |NS|∗|g[n][m]|>eps/(27∗n max)
            if |NS|∗|g[n][m]|∗|s[n][1]|>eps/(27∗n max)
               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 mul-

$$\hat{K}^{\mathrm{CMO}}\chi_i^{\mathrm{CMO}}(x)$$
$$=\sum_{\mu}^{n_{\mathrm{occ}}}\chi_\mu^{\mathrm{CMO}}(x)\int dx'\frac{\chi_\mu^{\mathrm{CMO}\dagger}(x')\chi_i^{\mathrm{CMO}}(x')}{|x-x'|},$$
$$=\sum_{j}^{n_{\mathrm{occ}}}U_{ji}^{*}\sum_{\mu}^{n_{\mathrm{occ}}}\chi_\mu^{\mathrm{LMO}}(x)\int dx'\frac{\chi_\mu^{\mathrm{LMO}\dagger}(x')\chi_j^{\mathrm{LMO}}(x')}{|x-x'|}, \quad (20)$$
$$=\sum_{j}^{n_{\mathrm{occ}}}U_{ji}^{*}[\hat{K}^{\mathrm{LMO}}\chi_j^{\mathrm{LMO}}(x)].$$

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 $n_{\mathrm{occ}}\times n_{\mathrm{occ}}$ matrix of one-electron dipole integrals $\langle\chi_\mu^{\mathrm{CMO}}|\mathbf{r}|\chi_\nu^{\mathrm{CMO}}\rangle$, which are efficiently computed as inner products.

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

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

(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 $\epsilon_{\mathrm{nuc}}=10^{-6}$), 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 $r(\mathrm{MO})$] of 10^{-5} and 10^{-6}, respectively. For the Ca and Sr

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 $r(\mathrm{MO}) \leqslant 10^{-6}$ within the accuracy 10^{-6} hartree. There is no significant error within an expected accuracy between two smoothing parameters $\epsilon_{\mathrm{nuc}} = 10^{-6}$ and $\epsilon_{\mathrm{nuc}} = 10^{-7}$, as expected. The resulting total energies agree with the previous numerical calculations[26,27]

blocks (their Frobenius norm $>5\times10^{-k}$). 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, $\epsilon_{\mathrm{nuc}}=10^{-6}$, and the box size $L=60$ bohr. The seventh and ninth order multiwavelet bases were used with $r(\mathrm{MO})\leqslant3\times10^{-4}$. 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

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

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