

## Automatic Selection of Integral Thresholds by Extrapolation in Coulomb and Exchange Matrix Constructions

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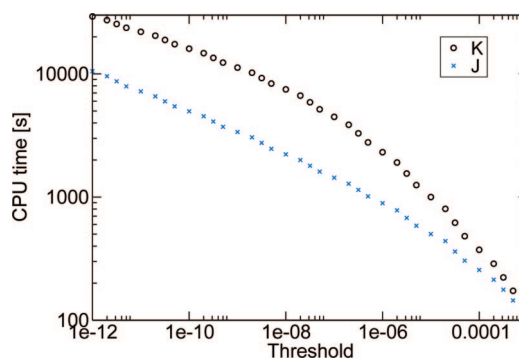
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**Abstract:** We present a method to compute Coulomb and exchange matrices with predetermined accuracy as measured by a matrix norm. The computation of these matrices is fundamental in Hartree-Fock and Kohn-Sham electronic structure calculations. We show numerically that, when modern algorithms for Coulomb and exchange matrix evaluation are applied, the Euclidean norm of the error matrix  $\varepsilon$  is related to the threshold value  $\tau$  as  $\varepsilon = c\tau^\alpha$ . The presented extrapolation method automatically selects the integral thresholds so that the Euclidean norm of the error matrix is at the requested accuracy. This approach is demonstrated for a variety of systems, including protein-like systems, water clusters, and graphene sheets. The proposed method represents an important step toward complete error control throughout the self-consistent field calculation as described in [*J. Math. Phys.* **2008**, 49, 032103].

### 1. Introduction

In large scale Hartree-Fock and Kohn-Sham electronic structure calculations, the Coulomb matrix  $J$  and the exchange matrix  $K$  are computed using various computational approximations for which threshold values must be chosen carefully in order to achieve a result of desired accuracy without performing unnecessary work. Cauchy-Schwarz screening of integrals and multipole approximations are frequently used to control errors in individual matrix elements  $\varepsilon_{ij}$ .<sup>1–10</sup> Such approximations are governed by a threshold value  $\tau$ : whenever a contribution to a matrix element is predicted to be smaller than  $\tau$ , that contribution is neglected. Thus, choosing a smaller  $\tau$  generally gives a more accurate result. However, smaller thresholds come with a performance penalty, affecting the timings by orders of magnitude—see Figure 1. One faces here a tradeoff between accuracy and performance. Therefore, the value of  $\tau$  has to be selected with care.

In practice, it is preferable to control the error in the entire matrix rather than individual contributions. Recently, it has been found that controlling the accuracy in the electron density amounts to controlling the Euclidean norm of the



**Figure 1.** The CPU time needed to evaluate Coulomb and exchange matrices as functions of the threshold value  $\tau$ . These are example timings measured for a HF/3–21G calculation on an insulin molecule.

error matrix for each approximation.<sup>11</sup> The Euclidean norm of a matrix  $A$  is defined as  $\|A\|_2 = \max_{\|x\|_2=1} \|Ax\|_2$ . The self-consistent field iterations are in ref 11 seen as a sequence of rotations of the occupied subspace, which uniquely defines the electron density for a given basis set. Errors coming from computational approximations, such as Cauchy-Schwarz screening of integrals and multipole approximations, are characterized as erroneous rotations. An erroneous rotation can be quantified by the canonical angles  $\Theta(\mathcal{X}, \mathcal{X})$  between

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the exact subspace  $\mathcal{X}$  and the perturbed subspace  $\tilde{\mathcal{X}}$ . Using matrix perturbation theory,<sup>16,17</sup> we show in ref 11 that controlling an erroneous rotation, as measured by the canonical angles, amounts to controlling the Euclidean norm of the error matrix  $E$  and knowing the band gap  $\xi$ :

$$\|\sin \Theta(\mathcal{X}, \tilde{\mathcal{X}})\|_2 \leq \frac{\|E\|_2}{\xi - \|E\|_2} \quad (1)$$

The band gap  $\xi$  can be efficiently computed as a byproduct of density matrix purification.<sup>12</sup> Provided that the norms of the error matrices can be controlled, all approximations can be governed by a single parameter, specifying the desired accuracy in the electron density, thus eliminating the need for ad-hoc chosen threshold values. See ref 11 for details. Along the lines of ref 11, we have previously presented truncation strategies for density matrix purification based on analytical error bounds of the canonical angles between exact and perturbed subspaces.<sup>18</sup> In this article, we aim to provide a method for similar control of the Coulomb and exchange matrix calculations.

One possible way of attacking this problem is using the Frobenius norm: the above-mentioned methods for screening away individual contributions can be used to compute upper bounds of the error in matrix elements, provided that the number of neglected contributions is accounted for. These upper bounds  $\varepsilon_{ij}$  are in turn related to the error in the total matrix using the Frobenius norm

$$\|E\|_F = \sqrt{\sum_{ij} \varepsilon_{ij}^2} \quad (2)$$

Formally, the Frobenius norm  $\|E\|_F$  could be used to estimate the Euclidean norm  $\|E\|_2$  for a matrix  $E$  of size  $n$  using

$$\frac{1}{\sqrt{n}} \|E\|_F \leq \|E\|_2 \leq \|E\|_F \quad (3)$$

Such estimation is however too loose for practical use, at least for large systems. Also, useful upper bounds of error matrix elements  $\varepsilon_{ij}$  may be difficult to come by. These difficulties cause the screening methods to be used in a qualitative way only: different screening thresholds are tried empirically until working ones are found. Such an approach does not guarantee scalability to larger systems.

In this article, we present a method to determine the relationship between the threshold value and the Euclidean norm of the error matrix in an automatic fashion, using extrapolation. Our method can be executed at run-time to select integral thresholds for  $J$  and  $K$ . These thresholds will be sufficiently tight to not obstruct the SCF convergence while requiring only necessary work.

## 2. Interaction Screening in Point Charge Model

In order to understand better the screening process, we study a simplified, classical model consisting of  $N$  discrete charges  $\{\rho_i\}$  with coordinates  $\{r_i\}$ . We consider computation of the potential generated by such a charge distribution, when ignoring in the computations contributions smaller than a threshold value  $\tau$ . Our goal is to find out how the error

introduced in the screening process depends on  $\tau$ . We choose the charges to have nonuniform distributions. It has been found that the distribution of density matrix elements for a nonconducting material follows an exponential function.<sup>21</sup> Therefore, we consider first the distribution  $\rho_i = e^{-\gamma x_i}$  where  $x_i$  are random numbers uniformly distributed in the  $[0, 1]$  interval and  $\gamma$  is a parameter determining the spread of the distribution. The expression for the Coulomb potential  $V_p$  measured at  $R_p$  is

$$V_p = \sum_{i=1}^N \frac{\rho_i}{|r_i - R_p|} \quad (4)$$

We insert the formula for  $\rho_i$  to obtain the screening error which we define as the normalized sum of all ignored contributions:

$$\varepsilon_p(\tau) = \frac{1}{N} \sum_{i=1}^N \begin{cases} \frac{\exp(-\gamma x_i)}{|r_i - R_p|}, & \frac{\exp(-\gamma x_i)}{|r_i - R_p|} < \tau \\ 0, & \frac{\exp(-\gamma x_i)}{|r_i - R_p|} \geq \tau \end{cases} \quad (5)$$

For large values of  $N$ , we can approximate the value of  $\varepsilon_p(\tau)$  with an integral over the variable  $x$ . Let us also assume that all denominators are of the same order and do not affect substantially the screening process and can therefore be moved out of the integration  $|r_i - R_p| \approx P_p$ . We get

$$\varepsilon_p(\tau) \approx \frac{1}{P_p} \int_{\exp(-\gamma x) P_p < \tau} e^{-\gamma x} dx = \frac{1}{P_p} \int_{\log((P_p \tau)^{-1/\gamma})}^1 e^{-\gamma x} dx \quad (6)$$

$$= \frac{1}{P_p} \left[ -\frac{1}{\gamma} e^{-\gamma x} \right]_{\log((P_p \tau)^{-1/\gamma})}^1 \quad (7)$$

$$= \frac{1}{P_p \gamma} [P_p \tau - e^{-\gamma}] \quad (8)$$

The second term  $e^{-\gamma}$  is the smallest charge present in the system. We can assume it is sufficiently small compared to the applicable values of  $\tau$  and interaction with it is always screened away. We then obtain a compact formula

$$\varepsilon_p(\tau) \approx \frac{1}{\gamma} \tau \quad (9)$$

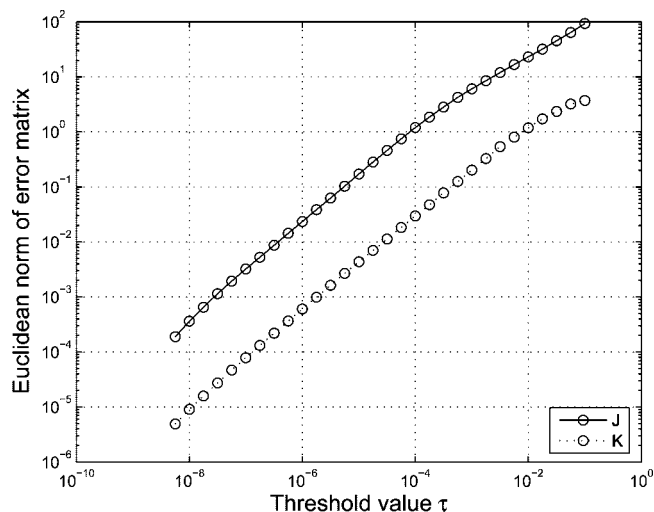
Let us repeat this derivation for another charge distribution. We take this time a set of random charges  $\rho_i = x_i^2$  where  $x_i$  are random numbers uniformly distributed in the  $[0, 1]$  interval. We make the same approximations as for the other charge distribution, that is assume that the denominator does not affect the screening, and that we can replace the discrete sum with an integral. We get the final expression

$$\varepsilon_p(\tau) \approx \frac{1}{P_p} \int_0^{x^2 P_p < \tau} x^2 dx = \frac{1}{3\sqrt{P_p}} \tau^{3/2} \quad (10)$$

A pattern can be observed: the screening error for both studied charge distributions has the form

$$\varepsilon(\tau) = c \tau^\alpha \quad (11)$$

where  $c$  and  $\alpha$  are some constants, and where the form of the charge distribution will affect the exponent  $\alpha$  of the formula. We note that the functional form in eq 11 is routinely used for numerical estimation of truncation errors



**Figure 2.** Errors versus threshold values for  $J$  and  $K$  matrix calculations on a water cluster containing 156 water molecules, using the 6-31G\*\* basis set. Matrices computed at  $\tau = 10^{-9}$  were used as reference for computing the error matrices.

in finite difference and finite element methods.<sup>22</sup> In that context, the expression is commonly written  $ch^\alpha$  where  $h$  is the mesh constant.

The presented interaction screening model can be used more or less directly to simulate the effects of screening on the Euclidean norm of the Coulomb error matrix. A particular charge distribution corresponds then to a magnitude distribution of density matrix elements. Simple-minded (4-center integral based) evaluation of the Coulomb matrix in turn corresponds to the pairwise evaluation of the classical potential as above. If we have used an orthogonal set of delta functions as the basis, the Coulomb matrix becomes diagonal, and the Euclidean norm of the error matrix can be computed exactly as the largest perturbation of the diagonal matrix elements. We have therefore a reason to presume that the screening error will behave as given by eq (11).

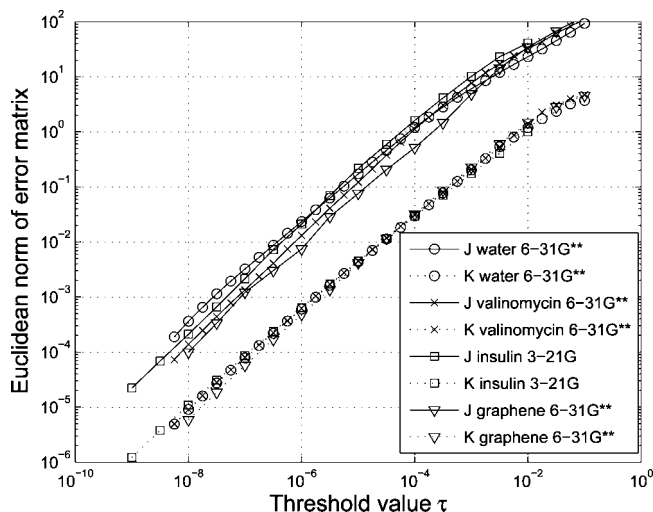
### 3. Numerical Error Estimates

After establishing the likely functional form of the error as given by eq (9), let us study the actual numerical error made in calculations of Coulomb and exchange matrices in Gaussian basis sets. We will consider the difference between the computed matrix  $J$  and the exact matrix  $J_{\text{exact}}$

$$E = J - J_{\text{exact}} \quad (12)$$

and analogously for  $K$ . We will refer to the matrix  $E$  as the *error matrix* and consider the Euclidean norm of  $E$ ,  $\varepsilon \equiv \|E\|_2$ . Once the relation  $\varepsilon(\tau)$  has been determined, its inverse  $\tau(\varepsilon)$  can be used to choose  $\tau$  so that the resulting error  $\varepsilon$  ends up at the requested accuracy.

Figure 2 shows the Euclidean norm of the error matrix for different values of  $\tau$  for computations of  $J$  and  $K$  for a water cluster containing 156 water molecules, using the 6-31G\*\* basis set. The calculations reported in this work were performed with the Ergo program,<sup>19,20</sup> with multipole approximations for the Coulomb matrix according to ref 8 and an algorithm for the exchange matrix essentially as



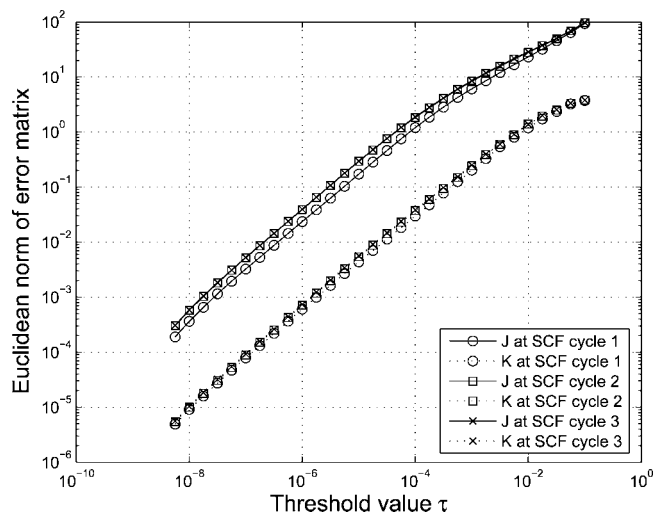
**Figure 3.** Errors versus threshold values for  $J$  and  $K$  matrix calculations for the four different test systems.

described in ref 3. Matrices calculated at  $\tau = 10^{-9}$  were used as reference for the computation of error matrices. For threshold values smaller than  $10^{-3}$  the logarithmic plot in Figure 2 is nearly linear for both  $J$  and  $K$ , indicating that the relationship between the threshold  $\tau$  and the error  $\varepsilon$  is of the form given by eq (11). Thus it appears that eq (11), which was derived for the Coulomb case, is also valid for the error in the exchange matrix. This is promising for our purposes here: once the values of the constants  $c$  and  $\alpha$  have been established, we can easily select the threshold value  $\tau$  so that the error in the computed Coulomb or exchange matrix is controlled

$$\tau(\varepsilon_{\text{req}}) = \left( \frac{\varepsilon_{\text{req}}}{c} \right)^{\frac{1}{\alpha}} \quad (13)$$

where  $\varepsilon_{\text{req}}$  is the requested accuracy when the error is measured as the Euclidean norm of the error matrix.

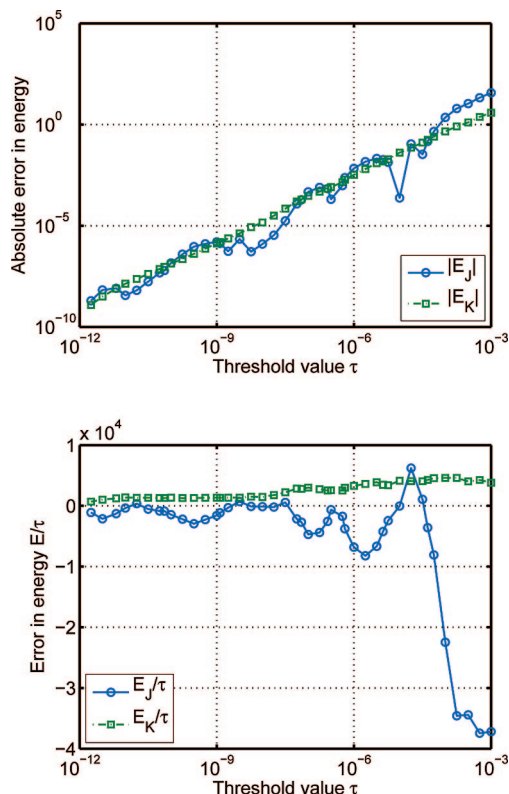
So far we have only seen that eq (11) is valid for one particular water cluster, for small enough values of  $\tau$ . It remains to investigate the relationship between  $\tau$  and  $\varepsilon$  for other systems, in order to see if our scheme is generally applicable. Figure 3 displays collected curves for a number of systems: same water cluster as above ( $\text{H}_{312}\text{O}_{156}$ ), valinomycin ( $\text{C}_{54}\text{N}_6\text{O}_{18}\text{H}_{90}$ ), insulin ( $\text{C}_{247}\text{N}_{62}\text{O}_{74}\text{S}_6\text{H}_{367}$ ), and a small graphene sheet ( $\text{C}_{96}\text{H}_{24}$ ). In all cases the behavior of the error with respect to the threshold value  $\tau$  is essentially in accordance with eq (11). However, the numbers  $c$  and  $\alpha$  vary somewhat for different systems. In our calculations, we get  $0.88 \leq \alpha \leq 1.00$ . This is close to the value  $\alpha = 1$  obtained in Section 2 for an exponential distribution of charges and thus agrees with earlier findings regarding the distribution of density matrix elements.<sup>21</sup> Values of  $c$  are implementation-dependent. Therefore, in order to control errors using eq (13), practical implementations should investigate the behavior of errors for the particular system and basis set in question. If we assume that the functional form in eq (11) is valid in all cases, it is sufficient to calculate three matrices using different threshold values in order to find values for the constants  $c$  and  $\alpha$ : the most accurate calculation is used as reference, while the two others provide two points on the graph



**Figure 4.** Errors versus threshold values for a Hartree-Fock calculation on a water cluster containing 156 water molecules, using the 6-31G\*\* basis set. Matrices computed at  $\tau = 10^{-9}$  were used as reference for computing the error matrices. Results for self-consistent field cycles 1, 2, and 3 are shown. There is some change going from cycle 1 to 2, while the results for cycle 3 are essentially the same as for cycle 2.

allowing for calculation of  $c$  and  $\alpha$ . Figure 3 suggests that the three calculations needed to determine the error behavior can be done at rather low accuracy, since the graphs appear linear already for thresholds  $\tau$  as large as  $10^{-3}$ . Thus, these three calculations will be relatively cheap if high accuracy is needed in the final result.

We have also investigated how the behavior of errors changes during the self-consistent field iterations. Figure 4 shows the error behavior for the same water cluster as in Figure 2, but this time for three self-consistent field cycles. The calculation was performed at the Hartree-Fock level with basis set 6-31G\*\*, with a starting guess density projected from a previous 3-21G calculation. There is a significant difference between the electron density in the first cycle compared to the second cycle, with the density affecting the offset  $c$  but leaving the slope  $\alpha$  virtually unchanged. This has an effect on the error behavior: errors are somewhat smaller in the first iteration compared to the second. However, in the third iteration (and in all subsequent iterations) the error curves are essentially the same as for the second iteration. Therefore, performing three calculations of  $J$  and  $K$  to assess the error behavior in cycle 2 would in this case provide values for the constants  $c$  and  $\alpha$  that would be valid in all subsequent iterations. Our test calculations on other systems show similar trends regarding the changes in different self-consistent field cycles: only the first cycle gives a change in density large enough to have a significant effect on the behavior of errors in the  $J$  and  $K$  matrices, when the starting guess is taken from a 3-21G calculation. This is good news from a performance point of view: since a self-consistent field calculation typically requires at least 5–10 iterations, the extra effort needed to find values for  $c$  and  $\alpha$  becomes only a small fraction of the total time since those values can then be reused throughout the whole self-consistent field calculation.



**Figure 5.** The error in the Coulomb and exchange energies as a function of the screening parameter  $\tau$ . The values have been obtained for the first SCF cycle of a HF/6-31G\*\* calculation on the valinomycin molecule. The same density matrix was used for all values of  $\tau$ . The upper panel displays the absolute values of the errors in the exchange and Coulomb energies. The lower displays the energy error divided by the corresponding threshold value.

#### 4. Selecting Threshold Values by Extrapolation

Based on the observations in the previous section, we propose the following scheme for error control in  $J$  and  $K$  matrix constructions: first, three low-accuracy matrix evaluations  $X_{i=1,2,3}$ ,  $X \in \{J, K\}$  are done in order to assess the error behavior, where different indices correspond to calculations with different threshold values  $\tau_{i=1,2,3}$ . The CPU time required to evaluate these matrices is only a small fraction of the CPU time required for a high-accuracy evaluation, see Figure 1. An optimized code could accelerate the process even further by computing all three at once rather than doing three separate matrix evaluations. Next, error matrices  $E_{j=1,2}$  are computed and the coefficients  $c$  and  $\alpha$  can be determined:

$$E_1 = X_3 - X_1, E_2 = X_3 - X_2 \quad (14)$$

$$\alpha = \frac{\log \|E_2\| - \log \|E_1\|}{\log \tau_2 - \log \tau_1}, c = \|E_1\| \tau_1^{-\alpha} \quad (15)$$

Having evaluated the parameters  $c$  and  $\alpha$  and given the requested accuracy  $\epsilon_{req}$  of the matrices in the norm of choice, the integral threshold can be trivially determined from eq (13). Provided that the density is reasonably close to convergence, this assessment of errors and evaluation of  $c$  and  $\alpha$  constants needs to be done only once, so that the



matrices can thereafter be computed with a requested accuracy using eq (13). Although our approach is not based on analytical error bounds, it is in practice applicable to most systems of interest; apart from the systems described above, we have also investigated water clusters of sizes varied between 9 and 156 water molecules and polypeptide helices of sizes between 54 and 418 atoms as well as different basis sets of double- and triple-zeta quality with and without polarization functions. We have not encountered any case where the behavior of errors in approximate Coulomb and exchange matrices is not well described by eq (11). In early iterations, when the density still changes a lot in each step, the extrapolation can be performed in every SCF step or since the choice of threshold values is less critical at that stage, transferred from previous cycles. After a few steps, when the structure of the density matrix has stabilized, the extrapolation coefficients can be straightforwardly reused. Generally, as seen in Figure 3, the differences in  $c$  and  $\alpha$  for different systems are not very large.

It is worth noting that at the same threshold value, the error in the exchange matrix is in our implementation 1–2 orders of magnitude lower—it is therefore beneficial to use different thresholds for Coulomb and exchange calculations. In general, the error in the exchange matrix depends in a remarkably predictable fashion on the chosen threshold value. The errors for the Coulomb matrix display some scatter of the  $c$  value, but the slope  $\alpha$  remains practically the same.

The scheme for selecting threshold values for computation of the matrices  $J$  and  $K$  proposed here may also be applicable to computation of the exchange-correlation matrix in Kohn-Sham calculations, provided that the accuracy is governed by one continuous parameter. The hierarchical cubature grid generation scheme developed by Challacombe<sup>23</sup> may be suitable for this, since it needs only a single parameter to determine the quality of the grid.

## 5. Concluding Remarks

We present an adaptive method for choosing the screening threshold in calculation of the Coulomb and exchange matrices. This method can be directly incorporated into the single-threshold SCF scheme proposed in ref 11.

The scheme for Coulomb and exchange matrix error control presented in this work does not make any assumptions about the actual calculation method of  $J$  and  $K$  matrices apart from ability to control its accuracy with a single threshold. It is important to note that the precise positions and slopes of the error curves presented in this article are dependent on details in the specific implementation; for example if screening of integrals is done for basis function products or for products of Gaussian primitives. Parameters such as box sizes and maximum order of multipole expansions may also affect the results. Thus, values for the constants  $c$  and  $\alpha$  should be determined separately for each implementation. We also note that for the proposed scheme to work for multipole methods, the method must be such that a single threshold value governs the accuracy, with the maximum degree of multipole expansion being a parameter affecting performance but not limiting the accuracy.<sup>5–8</sup>

Since many SCF optimization schemes are based on the energy,<sup>13–15</sup> it is tempting to select thresholds by extrapolation based on the errors in Coulomb and exchange energies. Unfortunately, the Coulomb energy, as computed in our implementation, behaves unpredictably as a function of  $\tau$ , see Figure 5. Therefore extrapolation based on the Coulomb energy seems difficult.

The presented method allows us to automatically select threshold values to control the error in the Coulomb and exchange matrices given some desired accuracy  $\|E\|_2 < \varepsilon_{\text{req}}$ . The requested accuracy  $\varepsilon_{\text{req}}$  should be determined from the band gap and the desired accuracy in the electron density as described in ref 11. Using that strategy for error control, the matrices are computed accurately enough to ensure convergence, but, at the same time, the performance is not hampered by excessively tight thresholds. We have recently presented analytical error bounds with accompanying truncation strategies for density matrix purification.<sup>18</sup> Combined with the present work this will allow for self-consistent field calculations without need for ad-hoc chosen threshold values.

Finally, we would like to stress that the presented extrapolation scheme is based on on-the-fly numerical error estimates. Achieving strict error control based on analytical error bounds for Coulomb and exchange matrix construction remains an open challenge.

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