

Nonmonotonic Recursive Polynomial Expansions for Linear Scaling Calculation of the Density Matrix

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ABSTRACT: As it stands, density matrix purification is a powerful tool for linear scaling electronic structure calculations. The convergence is rapid and depends only weakly on the band gap. However, as will be shown in this letter, there is room for improvements. The key is to allow for nonmonotonicity in the recursive polynomial expansion. On the basis of this idea, new purification schemes are proposed that require only half the number of matrix–matrix multiplications compared to previous schemes. The speedup is essentially independent of the location of the chemical potential and increases with decreasing band gap.

During the last two decades, methods have been developed that make it possible to apply electronic structure calculations, using Hartree–Fock, Kohn–Sham density functional theory, or tight-binding models, to systems with many thousands of atoms.^{1–5} Although the computational cost of these methods increases only linearly with system size, such calculations are extremely demanding. Therefore, there is a need to improve existing linear scaling methods in order to reduce the computational cost and make best use of modern computer resources.

In linear scaling electronic structure calculations, efficient computation of the one-particle density matrix D for a given effective Hamiltonian F is an important ingredient. Many methods for linear scaling computation of the density matrix have been proposed. A common approach is to employ a polynomial expansion of the function $D = \theta(\mu I - F)$, where θ is the Heaviside step function and μ is the chemical potential. The expansion may be built up serially by a Chebyshev series^{6–9} or recursively by density matrix purification^{10–14} or sign matrix methods.^{15,16} Another approach is to minimize an energy functional with respect to the density matrix.^{17–20}

For the isolated problem of computing the density matrix for a fixed Hamiltonian, the recursive density matrix purification schemes are highly efficient. The convergence is rapid, and the computational cost scales as $\mathcal{O}(\ln(\Delta\varepsilon/\xi))$, where $\Delta\varepsilon$ is the spectral width of the effective Hamiltonian matrix and ξ is the band gap.^{11,21} This should be compared to an $\mathcal{O}((\Delta\varepsilon/\xi)^{1/2})$ cost for the serial polynomial expansion⁹ and minimization^{1,21} methods. However, despite the excellent performance of previously proposed density matrix purification schemes, substantial improvements are still possible, as will be shown in this letter.

In density matrix purification, the effective Hamiltonian matrix is first shifted and scaled so that the eigenvalues end up in the $[0, 1]$ interval in reverse order. After that, low order polynomials with fixed points at 0 and 1 are recursively applied to build up the desired step function. The general iterative procedure can be formulated as

$$\begin{aligned} X_0 &= f_0(F) \\ X_i &= f_i(X_{i-1}), i = 1, 2, \dots \end{aligned} \quad (1)$$

where f_0 is the initial linear transformation and f_i , $i = 1, 2, \dots$ is a

sequence of low order polynomials. The iterative procedure is stopped as soon as all eigenvalues of X_i are sufficiently close to their desired values of 0 and 1. The stopping criterion can for example be set in terms of the last eigenvalues to converge,²² but other criteria are possible as well.^{10,14}

Purification can either be carried out with fixed or varying chemical potential μ . In the case of fixed- μ purification, a single polynomial with an unstable fixed point in $]0, 1[$ is typically used for all f_i , $i > 0$. The initial transformation f_0 maps the chemical potential to the unstable fixed point. The purification process then brings the eigenvalues to their desired values of 0 and 1. In the case of varying- μ purification, the chemical potential is allowed to move during the iterations. This flexibility can be used to automatically adjust the expansion so that the correct number of electrons is obtained, as in canonical¹⁰ and trace-correcting¹¹ purification.

In any case, the idea has been to use polynomials that increase monotonically in $[0, 1]$ and have fixed points and vanishing derivatives at 0 and 1. As discussed by Niklasson,¹¹ it can be understood that a recursive expansion using such polynomials will converge toward a step function. In the following, we shall use the notation $P_{ij}(x)$ for the polynomial of degree $1 + i + j$ with fixed points at 0 and 1 and with i and j vanishing derivatives at 0 and 1, respectively. Many previously proposed purification polynomials can be written in this form.²³

In this letter, we withdraw from the idea of using monotonically increasing purification polynomials. A scale and fold technique giving nonmonotonic purification transformations is proposed that results in improved performance of both fixed- and varying- μ purification schemes. The new idea is the following: Before each iteration, the eigenspectrum is stretched out outside the $[0, 1]$ interval. Some of the polynomials of the form P_{ij} can then be used to fold the eigenspectrum over itself. For example, the polynomial $P_{1,0}(x) = x^2$ can be used to fold the unoccupied part of the eigenspectrum if the eigenspectrum is stretched out below 0 before its application. Similarly, the polynomial $P_{0,1}(x) = 2x - x^2$ can be used to fold the occupied part. In general, the scale and fold technique can for a polynomial P_{ij} be used for the unoccupied part if i is odd and for the occupied part if j is odd.

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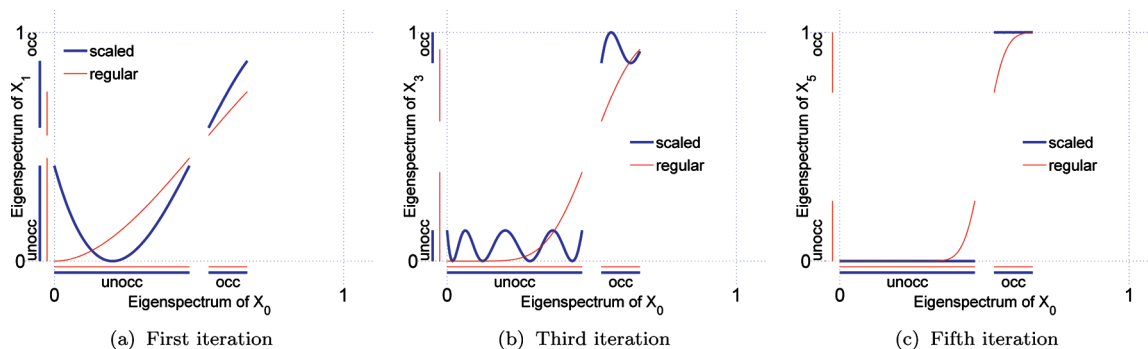


Figure 1. Mapping of the eigenspectrum after 1, 3, and 5 iterations of McWeeny based fixed- μ purification with and without the use of scaling. In this illustrative example, $\Delta\epsilon/\xi = 10$, and the chemical potential μ is located at $\lambda_{\min} + 0.25(\lambda_{\max} - \lambda_{\min})$.

Similar scaling techniques have previously been employed to improve the convergence of Newton iterations for sign matrix evaluations.^{24,25} However, in this case, the regular unscaled iteration keeps the eigenvalues outside the interval, and the scaling is used to shrink rather than stretch out the eigenspectrum.

We will first apply the scale and fold technique to fixed- μ purification using a polynomial $P_{m,m}$ with m being odd. For such polynomials, the technique can be used to fold both the unoccupied and occupied parts of the eigenspectrum in each iteration. In this case, the nonmonotonic purification transformation

$$f_i(X_{i-1}) = P_{m,m}(\alpha(X_{i-1} - 0.5I) + 0.5I) \quad (2)$$

where $\alpha \geq 1$, determines the amount of scaling around the unstable fixed point at 0.5. The complete algorithm for the special case $m = 1$ is given in Algorithm 1, where λ_{\min} and λ_{\max} are the extremal eigenvalues of F or bounds thereof. For simplicity, it is assumed here that the band gap is located symmetrically around μ . The expression for α can be derived by solving

$$P_{m,m}(\alpha(\beta - 0.5) + 0.5) = P_{m,m}(0.5(1 - \alpha)) \quad (3)$$

for $\alpha \geq 1$. Here, β is a parameter depending on the eigenvalue closest to 0.5, see Algorithm 1. The behavior of Algorithm 1 is illustrated in Figure 1 for a case with $\Delta\epsilon/\xi = 10$ and $\mu = \lambda_{\min} + 0.25(\lambda_{\max} - \lambda_{\min})$. The behavior of the regular grand-canonical purification algorithm,¹⁰ corresponding to Algorithm 1 with $\alpha = 1$, is shown for reference. Note how the scaled variant is able to take advantage of the additional flexibility given by allowing for nonmonotonicity, resulting in much faster convergence. Fixed- μ purification schemes with scaling can also be derived for other polynomials of the form P_{ij} , where i and j are both odd and larger than 0. Note that the scaling should be performed around the unstable fixed point of the polynomial, which will differ from 0.5 if $i \neq j$.

Algorithm 1. McWeeny-Based Fixed- μ Purification

Input: F , λ_{\min} , λ_{\max} , μ , ξ
 1: $\gamma = 2\max(\lambda_{\max} - \mu, \mu - \lambda_{\min})$
 2: $X_0 = (\mu I - F) / \gamma + 0.5I$
 3: $\beta = 0.5(1 - \xi/\gamma)$
 4: **for** $i = 1, 2, \dots, n$, **do**
 5: $\alpha = 3 / (12\beta^2 - 18\beta + 9)^{1/2}$
 6: $X_s = \alpha(X_{i-1} - 0.5I) + 0.5I$
 7: $X_i = 3X_s^2 - 2X_s^3$
 8: $\beta_s = \alpha(\beta - 0.5) + 0.5$
 9: $\beta = 3\beta_s^2 - 2\beta_s^3$
 10: **end for**
 11: **return** $D = X_n$

The scale and fold technique can also be used together with varying- μ purification. We shall here focus on purification based on the polynomials $P_{0,1}$ and $P_{1,0}$.²⁶ These polynomials can be used to adjust the occupation count:¹¹ if the occupation is too high, the $P_{1,0}$ polynomial is applied; otherwise, $P_{0,1}$ is applied. The scaling should in this case be chosen to stretch out the eigenspectrum below 0 before application of x^2 and above 1 before application of $2x - x^2$. The purification transformations are

$$f_i(X_{i-1}) = P_{1,0}(\alpha X_{i-1} + (1 - \alpha)I) \quad (4)$$

and

$$f_i(X_{i-1}) = P_{0,1}(\alpha X_{i-1}) \quad (5)$$

where $\alpha \geq 1$ determines the amount of scaling. A complete algorithm is given in Algorithm 2, where λ_{lumo} and λ_{homo} are the eigenvalues closest above and below the band gap, respectively, and n_{occ} is the number of occupied orbitals. Without scaling, i.e., $\alpha = 1$, this algorithm is equivalent to the second order trace correcting purification scheme by Niklasson.¹¹ The choice of polynomial on line 5 of the algorithm is based on the trace of the current density matrix approximation, just as in the original trace correcting scheme. However, other ways to choose the polynomial can be used as well.^{22,27} The behavior of Algorithm 2 is illustrated in Figure 2. The regular scheme with $\alpha = 1$ is shown for reference.

Algorithm 2. $P_{0,1}$ and $P_{1,0}$ -Based Varying- μ Purification

Input: F , n_{occ} , λ_{\min} , λ_{\max} , λ_{lumo} , λ_{homo}
 1: $X_0 = f_0(F) = (\lambda_{\max}I - F) / (\lambda_{\max} - \lambda_{\min})$
 2: $\beta = f_0(\lambda_{\text{lumo}})$
 3: $\bar{\beta} = f_0(\lambda_{\text{homo}})$
 4: **for** $i = 1, 2, \dots, n$, **do**
 5: **if** $\text{Tr}[X_{i-1}] > n_{\text{occ}}$, **then**
 6: $\alpha = 2 / (2 - \beta)$
 7: $X_i = (\alpha X_{i-1} + (1 - \alpha)I)^2$
 8: $\beta = (\alpha\beta + 1 - \alpha)^2$
 9: $\bar{\beta} = (\alpha\bar{\beta} + 1 - \alpha)^2$
 10: **else**
 11: $\alpha = 2 / (1 + \bar{\beta})$
 12: $X_i = 2\alpha X_{i-1} - \alpha^2 X_{i-1}^2$
 13: $\beta = 2\alpha\bar{\beta} - \alpha^2\bar{\beta}^2$
 14: $\bar{\beta} = 2\alpha\beta - \alpha^2\beta^2$
 15: **end if**
 16: **end for**
 17: **return** $D = X_n$

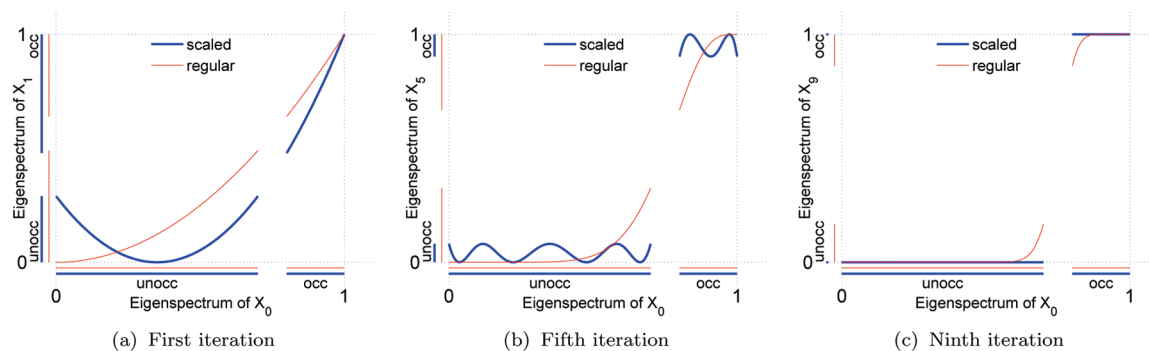


Figure 2. Mapping of the eigenspectrum after 1, 5, and 9 iterations respectively of $P_{0,1}$ - and $P_{1,0}$ -based varying- μ purification with and without the use of scaling. In this illustrative example, $\Delta\epsilon/\xi = 10$, and the chemical potential μ is located at $\lambda_{\min} + 0.25(\lambda_{\max} - \lambda_{\min})$.

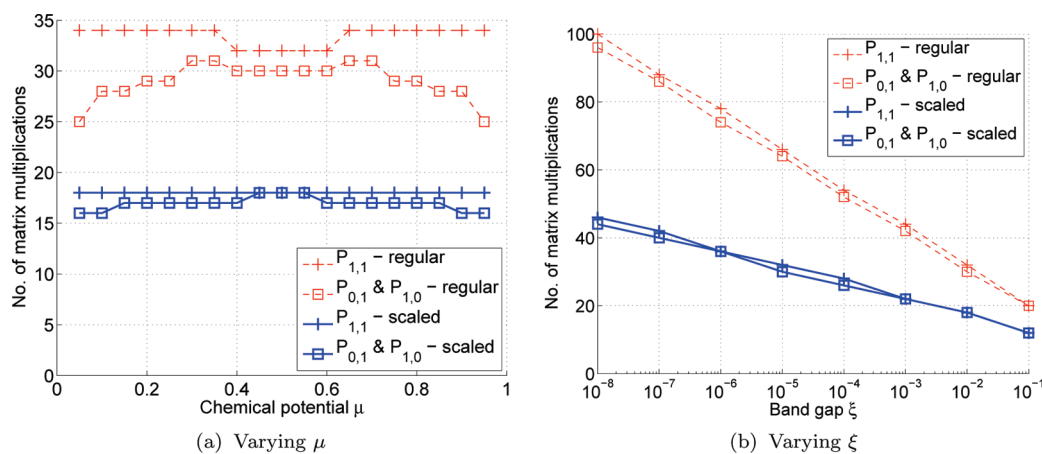


Figure 3. Number of matrix–matrix multiplications needed to reach an accuracy of $\|\tilde{D} - D\|_2 \leq 10^{-9}$, where \tilde{D} is the computed approximation of the exact density matrix D . The test calculations presented in panel a were performed on test Hamiltonians with band gaps $\xi = 0.01$ and varying chemical potential μ . The test calculations presented in panel b were performed on test Hamiltonians with chemical potentials $\mu = 0.5$ and varying band gap ξ . In all cases, the spectral widths of the test Hamiltonians were $\Delta\epsilon = 1$. The test cases in panel a are essentially equivalent to the test cases presented in Figure 2 of ref 11.

Figures 1 and 2 show that the use of scaling results in more rapid convergence. In order to closer study the performance enhancement given by the scaling technique, we shall consider diagonal test Hamiltonians with varying chemical potentials and band gaps. As previously discussed by Mazziotti,¹⁴ the results for a given chemical potential and a given band gap are valid for any Hamiltonian with that band gap and chemical potential.

Figure 3a shows that the proposed scaling techniques give significant speedup independently of the location of the chemical potential. As can be seen in Figure 3b, the costs of the scaled purification schemes scale as $\mathcal{O}(\ln(1/\xi))$ with the band gap ξ , just as for the regular schemes. However, the convergence for the scaled schemes is around twice as fast as for the regular schemes.

The scaling technique requires some information about the band gap. More precisely, a lower bound of the lower edge and an upper bound of the upper edge of the band gap are needed. These bounds can be used in place of λ_{homo} and λ_{lumo} in Algorithm 2. It should be noted that incorrect bounds can lead to a mix-up between occupied and unoccupied states. However, even if the bounds are not tight, the scaling technique can be used, although the effect will not be as good as it could have been.

Tight bounds can be obtained by some technique for calculation of interior eigenvalues.^{22,28,29}

The performance was here measured by the number of matrix–matrix multiplications needed to reach a certain accuracy. In practical linear scaling calculations, an efficient way to bring about sparsity is critical for the performance. Since the proposed schemes are on the standard form given by eq 1, it is possible to combine them with previously suggested schemes to control the forward error.²² To achieve forward error control, information about the band gap is needed. Fortunately, this is the same information as needed for the proposed scaling techniques.

In this letter, nonmonotonic recursive polynomial expansions for calculation of the density matrix were proposed. We have withdrawn from the idea that the approximation of the step function should be monotonically increasing and show that this makes it possible to find new, more efficient nonmonotonic purification transformations. The scaled purification variants of this work represent a substantial improvement compared to previous purification schemes. The reduction in computational cost is essentially independent of the location of the chemical potential, and the proposed schemes are particularly efficient in the case of small band gaps.

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- (23) The McWeeny polynomial³⁰ is $P_{1,1}(x) = 3x^2 - 2x^3$. This polynomial is equivalent to the Newton–Schulz iteration polynomial $\frac{1}{2}x(3 - x^2)$ for sign matrix evaluation.²⁵ The polynomials suggested by Holas¹³ can be written in the form $P_{m,m}(x)$. Niklasson¹¹ proposed purification schemes based on polynomials $P_{1,m}(x)$ and $P_{m,1}(x)$. Mazziotti¹⁴ suggested use of asymmetric polynomials $P_{m,m+1}(x)$ and $P_{m+1,m}(x)$.
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