Density Matrix Perturbation Theory

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An expansion method for perturbation of the zero temperature grand canonical density matrix is introduced. The method achieves quadratically convergent recursions that yield the response of the zero temperature density matrix upon variation of the Hamiltonian. The technique allows treatment of embedded quantum subsystems with a computational cost scaling linearly with the size of the perturbed region, $O(N_{\text{pert}})$, and as $O(1)$ with the total system size. It also allows direct computation of the density matrix response functions to any order with linear scaling effort. Energy expressions to 4th order based on only first and second order density matrix response are given.

In electronic structure theory, significant effort has been devoted to the development of methods with the computational cost scaling linearly with system size [1,2]. The ability to perform accurate calculations with reduced-complexity $O(N)$ scaling is an important breakthrough that opens a variety of new possibilities in computational materials science, chemistry and biology. One of the most elegant and efficient approaches to linear scaling is density matrix purification [3–9], where constructing the density matrix by quadratically convergent spectral projections replaces the single-particle eigenvalue problem arising in tight-binding and self-consistent Hartree-Fock and Kohn-Sham theory. For large insulating systems this method is efficient because of the sparse $O(N)$ real-space matrix representation of operators. Instead of cubic scaling, the computational cost scales linearly with the system size. Apart from $O(N)$ purification techniques there are alternative approaches such as constrained functional minimization [10,11], and hybrid schemes [12–16].

In this letter, we introduce a grand canonical density matrix perturbation theory based on recently developed spectral projection methods for purification of the density matrix [8,9]. The method provides direct solution of the zero temperature density matrix response upon variation of the Hamiltonian through quadratically convergent recursions. The method makes it possible to study embedded quantum subsystems and density matrix response functions within linear scaling effort. The density matrix perturbation technique avoids using wavefunction formalism. In spirit, it is therefore similar to the density matrix perturbation method proposed by McWeeny [17] and offers a flexibility comparable to Green’s function methods [18,19]. The present work is likewise related to the recent work of Bowler and Gillan [20], who developed a functionally constrained density matrix minimization scheme for embedding. However, our approach to computation of the density matrix response is quite different from existing methods of solutions for the coupled-perturbed self-consistent-field equations. In contrast to conventional methods that pose solution implicitly through coupled equations [21–24], the new method provides explicit construction of the derivative density matrix through recursion.

The main problem in constructing a density matrix perturbation theory is the non-analytic relation between the zero temperature density matrix and the Hamiltonian, given by the discontinuous step function [25],

$$ P = \theta[\mu I - H]. \quad (1) $$

This discontinuity makes expansion of $P$ about $H$ difficult. At finite temperatures the discontinuity disappears and we may use perturbation expansions of the analytic Fermi-Dirac distribution [26]. However, even at finite temperatures a perturbation expansion based on the Fermi-Dirac distribution may have slow convergence.

In linear scaling purification schemes [3–9], the density matrix is constructed by recursion:

$$
\begin{align*}
X_0 &= L(H), \\
X_{n+1} &= F_n(X_n), \quad n = 0, 1, 2, \ldots \\
P &= \lim_{n \to \infty} X_n.
\end{align*}
$$

(2)

Here, $L(H)$ is a linear normalization function mapping all eigenvalues of $H$ in reverse order to the interval of convergence [0, 1] and $F_n(X_n)$ is a set of functions projecting the eigenvalues of $X_n$ toward 1 (for occupied states) or 0 (for unoccupied states). In one of the simplest and most efficient techniques, which requires only knowledge of the number of occupied states $N_e$ and no a priori knowledge of $\mu$ [8], we have

$$ F_n(X_n) = \begin{cases} 
X_n^2, & Tr(X_n) \geq N_e \\
2X_n - X_n^2, & Tr(X_n) < N_e.
\end{cases} \quad (3) $$

Purification expansion schemes are quadratically convergent, numerically stable, and can even solve problems with degenerate eigenstates and fractional occupancy [9]. Thanks to an exponential decay of the density matrix elements as a function of $|r - r'|$ for insulating materials,
the operators have a sparse matrix representation and
the number of non-zero matrix elements above a numeri-
cal threshold scales linearly with the system size. In
these cases the matrix-matrix multiplications, which are
the most time consuming steps, have an $N$-scaling cost.

Equivalent to the purification schemes are the sign-
matrix expansions [27–29]. The general scheme is the
same as in Eq. (2), but the expansion is performed around
a step from $-1$ to $1$ at $x = 0$.

Our grand canonical density matrix perturbation the-
ory is based on the purification in Eq. (2). A perturbed
Hamiltonian $H = H^{(0)} + H^{(1)}$ gives the expansion
\[ X_n = X_n^{(0)} + \Delta_n, \quad n = 0, 1, 2, \ldots, \]
where $X_n^{(0)}$ is the unperturbed expansion and $\Delta_n$ are the
differences due to the perturbation $H^{(1)}$. It is then easy to show that
\[ \Delta_{n+1} = F_n(X_n^{(0)} + \Delta_n) - F_n(X_n^{(0)}) \]
\[ P = P^{(0)} + \lim_{n \to \infty} \Delta_n. \]
This is the key result of the present article and defines
our grand canonical density matrix perturbation theory.
Combining Eq. (5) with the expansion in Eq. (3) gives the recursive expansion [25]
\[ \Delta_{n+1} = \begin{cases} \{X_n^{(0)}, \Delta_n\} + \Delta_n^2 & \text{if } Tr(X_n^{(0)}) \geq N_e \\ 2\Delta_n - \{X_n^{(0)}, \Delta_n\} - \Delta_n^2 & \text{otherwise}. \end{cases} \]
Other expansions based on, for example, McWeeny, trace
conserving or trace resetting purification [3,5,9] can also be
included in this quite general approach. However,
Eq. (6) is particularly efficient since it only requires two
matrix multiplications per iteration. Because the pertur-
bation expansions inherit properties from their generator
sequence, they are likewise quadratically convergent with
iteration, numerically stable, and exact to within accu-
rracy of the drop tolerance [9].

If the perturbed $X_n^{(0)}$ has eigenvalues outside the in-
terval of convergence $[0, 1]$ the expansion could fail. To
avoid this problem the normalization function $L(H)$ in
Eq. (2) can be chosen to contract the eigenvalues of $X_0$
to $[\delta, 1 - \delta]$, where $\delta > 0$ is sufficiently large.

A major advantage with the expansion in Eq. (6) is that
for band-gap materials that are locally perturbed,
the $\Delta_n$ are likewise localized as a result of nearsighted-
ness [30,11]. The matrix products in Eq. (6) can therefore
be calculated using only the local regions of $X_n$ that re-
spond to the perturbation. Given that perturbation does
not change the overall decay of the density matrix, the
computational cost of the expansion scales linearly with
the size of the perturbed region $O(N_{\text{pert}})$ and as $O(1)$
with the total system size.

Density matrix purification does not necessarily re-
quire prior knowledge of the chemical potential, but once
the initial expansion of the unperturbed system is car-
rried out, the chemical potential is set. The perturbation
expansions of Eq. (5) are therefore grand canonical [31].
With this in mind, Eq. (6) may be readily applied to em-
bedding schemes that do involve long range charge flow.

The computation of many spectroscopic properties
such as the Raman spectra, chemical shielding and polar-
ization requires the calculation of density matrix deriva-
tives with respect to perturbation. Grand canonical den-
sity matrix perturbation theory can be used to compute
describe these response functions. Assume a perturbation of the
Hamiltonian $H^{(0)}$,
\[ H = H^{(0)} + \lambda H^{(1)}, \]
in the limit $\lambda \to 0$. The corresponding density matrix is
\[ P = P^{(0)} + \lambda P^{(1)} + \lambda^2 P^{(2)} + \ldots, \]
where the response functions $P^{(\mu)}$ (density matrix deriva-
tives) correspond to order $\mu$ in $\lambda$. Expanding the pertur-
bation as in Eq. (6), individual response terms may be
collected order by order at each iteration;
\[ \Delta_n = \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \ldots. \]
Keeping terms through order $m$ in $\lambda$ at each iteration,
with $\Delta_n^{(0)} = X_n$, the following recursive sequence is ob-
tained for $\mu = m, m - 1, \ldots, 1$:
\[ \Delta^{(\mu)}_{n+1} = \begin{cases} \sum_{i=0}^{\mu} \Delta^{(i)} \Delta^{(\mu-i)} & \text{if } Tr(X_n) \geq N_e \\ 2\Delta^{(\mu)} - \sum_{i=0}^{\mu} \Delta^{(i)} \Delta^{(\mu-i)} & \text{otherwise}. \end{cases} \]
These equations provide an explicit, quadratically con-
vergent solution of the response functions, where
\[ P^{(\mu)} = \lim_{n \to \infty} \Delta_n^{(\mu)}. \]
With the same technique it is possible to treat perturba-
tions where $H = H^{(0)} + \lambda_a H_a^{(1)} + \lambda_b H_b^{(1)} + \lambda_a \lambda_b H_{ab}^{(2)} + \ldots$
to produce a mixed density matrix expansion $P = P^{(0)} + \lambda_a P_a^{(1)} + \lambda_b P_b^{(1)} + \lambda_a \lambda_b P_{ab}^{(2)} + \ldots$.

Equation (10) provide direct explicit construction of the
response equations based on well developed linear
scaling technologies [8,9]. This is quite different from
conventional approaches [21–24] that pose solution im-
plicitly through coupled matrix equations, achieving at
best linear scaling with iterative solvers.

Higher order expansions of an observable can be cal-
culated efficiently from low order density matrix terms.
Similar to Wigner’s $2n+1$ rule for wavefunctions [32] we
have the energy response $E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \lambda^4 E^{(4)}$, where
\[ E^{(1)} = Tr(P^{(0)} H^{(1)}), \]
\[ E^{(2)} = 0.5 Tr(P^{(1)} H^{(1)}) \]
\[ E^{(3)} = 0.5 Tr([P^{(1)}, P^{(0)}] P^{(1)} H^{(1)}), \]
\[ E^{(4)} = 0.5 Tr([P^{(2)} - P^{(0)} P^{(1)} P^{(0)} P^{(1)} - P^{(0)} P^{(1)} P^{(2)} (I + P^{(0)}) H^{(1)}] P^{(1)} P^{(0)} P^{(0)} P^{(0)} P^{(1)} - P^{(0)} P^{(1)} P^{(2)} (I + P^{(0)}) H^{(1)}). \]
The corresponding n+1 rule for $\mu > 0$ is

$$E(\mu) = \mu^{-1} \text{Tr}(P^{(\mu-1)} H^{(1)}).$$

(13)

To demonstrate the grand canonical density matrix perturbation theory, we present two examples based on single-site perturbations of a model Hamiltonian and a beta-carotene molecule.

The model Hamiltonian has random diagonal elements exhibiting exponential decay of the overlap elements as a function of site separation on a randomly distorted lattice. This model represents a Hamiltonian of an insulator that might occur, for example, with a Gaussian basis set in density functional theory or in various tight-binding schemes. A local perturbation is imposed on the model Hamiltonian by moving the position of one of the lattice sites. Using the perturbation expansion of Eq. (6), a series of perturbations $\Delta_n$ is generated. In each step a numerical threshold $\tau = 10^{-6}$ is applied as described in [9]. The lower inset in Fig. 1 shows the number of elements above the threshold in $\Delta_n$ as a function of iteration. The local perturbation is efficiently represented with only $\sim 50$ elements out of $10^4$. Figure 1 also illustrates the quadratic convergence of the error. At convergence after $M$ iterations the new perturbed density matrix is given by $P = P^{(0)} + \Delta_M$. The error $\|P - P_{\text{exact}}\|_2 = 6.4 \times 10^{-5}$ and the error $|E - E_{\text{exact}}| = 1.3 \times 10^{-6}$ [34]. The error of the perturbed density matrix $P$ is stable at convergence and close to the numerical error for the unperturbed density matrix due to thresholding $\|P^{(0)} - P_{\text{exact}}^{(0)}\|_2 = 1.0 \times 10^{-4}$, and $|E^{(0)} - E_{\text{exact}}^{(0)}| = 2.4 \times 10^{-6}$.

The electronic structure of the second example, the beta-carotene molecule, was calculated with the MondoSCF suite of linear scaling algorithms [33] at the RHF/STO-2G level of theory. Figure 2 shows the matrix sparsity factor of the density matrix for beta-carotene. The difference between two fully self-consistent Fockians was chosen as a perturbation, (one with and one without a small displacement of a single carbon atom). In this way, more long-ranged effects due to self-consistency are included. Even if beta-carotene is too small to have a very sparse representation of the density matrix, the perturbation sequence $\Delta_n$ is found to be highly sparse. The error with threshold $\tau = 10^{-5}$ in the single-particle Hartree-Fock energy $|E - E_{\text{exact}}| = 2.8 \times 10^{-5}$ a.u., which is of the same order of error as for the unperturbed molecule. Standard first order perturbation theory yields an error two orders of magnitude larger [35].

The present formulation has been developed in an orthogonal representation. With a $N$-scaling congruence transformation [12], it is straightforward to employ this representation when using a non-orthogonal basis. When using a non-orthogonal basis set, change in the inverse overlap matrix $S^{-1}$ due to a local perturbation $dS$ is given by the recursive Dyson equation,

$$\delta_n+1 = S_0^{-1} dS(S_0^{-1} + \delta_n),$$

(14)

where $S = S_0 - dS$, $\delta_0 = 0$, and $S^{-1} = S_0^{-1} + \lim_{n \to \infty} \delta_n$. The equation contains only terms with local sparse updates and the computational cost scales linearly, $O(N_{\text{pert}})$, with the size of the perturbed region. Similar perturbation schemes for the sparse inverse Cholesky or square root factorizations can also be applied [36].

Density matrix perturbation theory can be applied in many contexts. For example, a straightforward calculation of the energy difference due to a small perturbation of a very large system may not be possible because of the numerical problem in resolving a tiny energy difference between two large energies. With density matrix perturbation theory, we work directly with the density matrix difference $\delta_n$ and the problem can be avoided, for example, the single particle energy change $\Delta E = \lim_{n \to \infty} \text{Tr}(H \Delta_n)$. In analogy to incremental Fock builds in self-consistent field calculations [39], the technique can be used in incremental density matrix builds. Connecting and disconnecting individual weakly interacting [40] quantum subsystems can be performed by treating off-diagonal elements of the Hamiltonian as a perturbation. This should be highly useful in nanoscience for connecting quantum dots, surfaces, clusters and nanowires, where the different parts can be calculated separately, provided a connection through a common chemical potential is given, for example via a surface substrate. In quantum molecular dynamics, such as quantum mechanical-molecular mechanical QM/MM schemes, or Monte-Carlo simulations, where only a local part of the system is perturbed and updated, the new approach is of interest. Several techniques used within the Green’s function context also should apply for the density matrix. The proposed perturbation approach may be used for response functions, impurities, effective medium and local scattering techniques [18,19,37,38]. The theory of grand canonical density matrix perturbation is thus a rich field with applications in many areas of materials science, chemistry and biology.

In summary, we have introduced a grand canonical perturbation theory for the zero temperature density matrix, extending quadratically convergent purification techniques to expansions of the density matrix upon variations of the Hamiltonian. The perturbation method allows the local adjustment of embedded quantum subsystems with a computational cost that scales as $O(1)$ for the total system size and as $O(N_{\text{pert}})$ for the region that respond to the perturbation, as demonstrated in Figs. 1 and 2. A new quadratically convergent $N$-scaling recursive approach to computing density matrix response functions has been outlined, and energy expressions to 4th order in terms of only first and second order density matrix response were given. The density matrix perturbation technique is surprisingly simple and offers an efficient alternative to several Green’s function meth-
ods and conventional schemes for solution of the coupled perturbed self-consistent-field equations.

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FIG. 1. The Error = log_{10}(||X_n^{(0)} + \Delta_n - P_{exact}||_2) as a function of iterations n (N = 100, N_c = 50). The lower inset shows the number of non-zero matrix elements of A above threshold r = 10^{-6}. The upper inset shows the density matrix perturbation.

FIG. 2. The matrix sparsity factors (number of non-zero elements over the total number of elements) for beta-carotene (RHF/STO-2G).
Error convergence in the perturbation expansion

Density matrix perturbation

Perturbation compression

log(Error)

Iteration

non-zero elements

Iteration

expansion
Beta Carotene, RHF/STO–2G

Matrix sparsity factor

Iteration

- $X_n$ Unperturbed sequence ($\tau=10^{-4}$)
- $\Delta_n$ Perturbation ($\tau=10^{-4}$)
- $X_n$ Unperturbed sequence ($\tau=10^{-5}$)
- $\Delta_n$ Perturbation ($\tau=10^{-5}$)