

Density Matrix Perturbation Theory

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An orbital-free quantum perturbation theory is proposed. It gives the response of the density matrix upon variation of the Hamiltonian by quadratically convergent recursions based on perturbed projections. 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. The method allows efficient high order perturbation expansions, as demonstrated with an example involving a 10th order expansion. Density matrix analogs of Wigner's $2n + 1$ rule are also presented.

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In electronic-structure theory, significant effort has been devoted to the development of methods with the computational cost scaling linearly with system size N [1,2]. The ability to perform calculations with reduced-complexity $O(N)$ scaling is an important breakthrough that opens a variety of new possibilities in materials science, chemistry, and biology. So far most attention has been focused on N -scaling methods for computing the ground state energy. A problem that has been given little attention is the $O(N)$ computation of response properties, for example, the polarizability, nuclear magnetic resonance, Raman intensities, vibrational frequencies, and the magnetic susceptibility [3]. Also of great interest is extending $O(N)$ electronic-structure theory to quantum embedding [4,5], where the computational complexity scales linearly with the size of a locally perturbed region $O(N_{\text{pert.}})$ and therefore as $O(1)$ with the total system size. This allows efficient studies of subsystems, for example, surface chemistries or the catalytic domains of proteins, without recalculation of the entire system.

In this Letter, we introduce a general and surprisingly simple $O(N_{\text{pert.}})$ approach to quantum perturbation theory. The method makes it possible to study embedded quantum subsystems and response functions to any order, within linear scaling effort. The approach is based on recently developed spectral projection schemes for purification of the density matrix, replacing the conventional eigenvalue problem in tight-binding or self-consistent Hartree-Fock and Kohn-Sham theories [6–13].

The orbital-free perturbation theory is based on the density matrix and avoids wave function or Green's function formalism [4,5]. In spirit, it is therefore similar to the perturbation method by McWeeny [14]. Our method is likewise related to the work of Bowler and Gillan [15], 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 previous methods of solutions for the coupled-perturbed self-consistent-field equations. In contrast to previous methods that pose a solution implicitly through coupled equations [16], 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 nonanalytic relation between the zero temperature density matrix and the Hamiltonian, given by the discontinuous step function [17],

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

which makes expansion of P about H difficult. At finite temperatures the discontinuity disappears, but instead the analytic Fermi-Dirac distribution involves problems with matrix exponentials and the chemical potential.

In linear scaling purification schemes [6–13], the density matrix is constructed by recursion;

$$\begin{aligned} X_0 &= L(H), \\ X_{n+1} &= F_n(X_n), \quad n = 0, 1, 2, \dots, \\ P &= \lim_{n \rightarrow \infty} X_n. \end{aligned} \quad (2)$$

Here, $L(H) = \alpha(\beta I - H)$ is a linear normalization function [17] 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). One of the most efficient techniques, which requires only a knowledge of the number of occupied states N_e and no *a priori* knowledge of μ [10], applies the projections

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

Purification projection schemes are quadratically convergent, numerically stable, and can solve problems even with degenerate eigenstates, finite temperatures, and fractional occupancy [11,13]. Thanks to an exponential decay of the density matrix elements as a function of $|\mathbf{r} - \mathbf{r}'|$ for insulating materials, the operators have a sparse matrix representation, and the number of nonzero matrix elements above a numerical threshold scales linearly with the system size [1,2]. In these cases the matrix-matrix

multiplications, which are the most time-consuming steps, scale $O(N)$.

Equivalent to the purification schemes are the sign-matrix expansions [18]. 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 quantum perturbation theory is based on the purification in Eq. (2). A perturbed Hamiltonian $H = H^{(0)} + H^{(1)}$ gives the expansion

$$X_n = X_n^{(0)} + \Delta_n, \quad n = 0, 1, 2, \dots, \quad (4)$$

where $X_n^{(0)}$ is the unperturbed expansion and Δ_n are the differences due to the perturbation $H^{(1)}$ [$\Delta_0 = L(H) - L(H^{(0)}) = -\alpha H^{(1)}$]. It is then easy to construct the perturbed projection expansion

$$\begin{aligned} \Delta_{n+1} &= F_n(X_n^{(0)} + \Delta_n) - F_n(X_n^{(0)}), \\ P &= P^{(0)} + \lim_{n \rightarrow \infty} \Delta_n. \end{aligned} \quad (5)$$

This is the key result of the present Letter and defines our density matrix perturbation theory. Combining Eq. (5) with the expansion in Eq. (3) gives the orbital-free recursive expansion [17]

$$\Delta_{n+1} = \begin{cases} \{X_n^{(0)}, \Delta_n\} + \Delta_n^2, & \text{if } \text{Tr}(X_n^{(0)}) \geq N_e, \\ 2\Delta_n - \{X_n^{(0)}, \Delta_n\} - \Delta_n^2, & \text{otherwise.} \end{cases} \quad (6)$$

Other expansions based on, for example, McWeeny, trace conserving or trace resetting purification [6,8,11] can also be included in this quite general approach. However, Eq. (6) is particularly efficient since it requires only two matrix multiplications per iteration. Because the perturbation expansions inherit properties from their generator sequence, they are likewise quadratically convergent with iteration, numerically stable, and exact to within accuracy of the drop tolerance [11].

If the perturbed $X_0^{(0)}$ has eigenvalues outside the interval 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 Δ_n are likewise localized as a result of nearsightedness [19,20]. The matrix products in Eq. (6) can therefore be calculated using only the local regions of X_n that respond 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 require prior knowledge of the chemical potential, but once the initial expansion of the unperturbed system is carried out, the chemical potential is set. The perturba-

tion expansions of Eq. (5) are therefore grand canonical [21]. With this in mind, Eq. (6) may be applied to embedding schemes that do involve long range charge flow.

The computation of many materials response properties requires the calculation of density matrix derivatives with respect to a perturbation. Grand canonical density matrix perturbation theory can be used to compute these response functions. Assume a perturbation of the Hamiltonian $H^{(0)}$,

$$H = H^{(0)} + \lambda H^{(1)}, \quad (7)$$

in the limit $\lambda \rightarrow 0$. The corresponding density matrix is

$$P = P^{(0)} + \lambda P^{(1)} + \lambda^2 P^{(2)} + \dots, \quad (8)$$

where the response functions $P^{(\gamma)}$ (density matrix derivatives) correspond to order γ in λ . Expanding the perturbation as in Eq. (6), individual response terms may be collected order by order at each iteration;

$$\Delta_n = \lambda \Delta_n^{(1)} + \lambda^2 \Delta_n^{(2)} + \dots \quad (9)$$

Keeping terms through order m in λ at each iteration, with $\Delta_n^{(0)} = X_n^{(0)}$, we obtain for $\gamma = m, m-1, \dots, 1$:

$$\Delta_{n+1}^{(\gamma)} = \begin{cases} \sum_{i=0}^{\gamma} \Delta_n^{(i)} \Delta_n^{(\gamma-i)}, & \text{if } \text{Tr}(X_n) \geq N_e, \\ 2\Delta_n^{(\gamma)} - \sum_{i=0}^{\gamma} \Delta_n^{(i)} \Delta_n^{(\gamma-i)}, & \text{otherwise.} \end{cases} \quad (10)$$

These equations give an explicit, quadratically convergent solution of the response functions, where

$$P^{(\gamma)} = \lim_{n \rightarrow \infty} \Delta_n^{(\gamma)}. \quad (11)$$

Mixed independent perturbation parameters can also be included.

Equation (10) provides direct explicit construction of the response equations based on well developed linear scaling technologies [10,11]. This is quite different from earlier approaches [16] that pose solution implicitly through coupled matrix equations, achieving at best linear scaling with iterative solvers. In a future publication we develop our theory for the solution of the coupled-perturbed self-consistent field equations [22].

Higher order expansions of the energy can be calculated efficiently from low order density matrix terms. Similar to Wigner's $2n+1$ rule for wave functions [23] we have the energy response $E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \lambda^4 E^{(4)}$, where

$$\begin{aligned} E^{(1)} &= \text{Tr}(P^{(0)} H^{(1)}), & E^{(2)} &= 0.5 \text{Tr}(P^{(1)} H^{(1)}), \\ E^{(3)} &= \text{Tr}([P^{(1)}, P^{(0)}] P^{(1)} H^{(1)}), \\ E^{(4)} &= 0.5 \text{Tr}([(2I - P^{(0)}) P^{(2)} P^{(0)} P^{(1)} \\ &\quad - P^{(0)} P^{(1)} P^{(2)} (I + P^{(0)})] H^{(1)}). \end{aligned} \quad (12)$$

The corresponding $n+1$ rule for $\gamma > 0$ is

$$E^{(\gamma)} = \gamma^{-1} \text{Tr}(P^{(\gamma-1)} H^{(1)}). \quad (13)$$

To demonstrate the perturbation theory, we present two examples: the first is based on a local perturbation of a model Hamiltonian, and the second example illustrates the ability to calculate higher order response functions.

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 perturbed projection expansion of Eq. (6), a series of perturbations Δ_n is generated. In each step a numerical threshold $\tau = 10^{-6}$ is applied as described in [11]. The lower inset in Fig. 1 shows the number of elements above the threshold in Δ_n as a function of iteration. The local perturbation is efficiently represented with only ~ 50 elements out of 10^4 . Figure 1 also illustrates the quadratic convergence and stability of the error. The error is close to the truncation error of the unperturbed density matrix and about 5000 times smaller compared to first order perturbation theory.

The second example, in Fig. 2, illustrates the perturbation of the Hamiltonian

$$H = -\frac{1}{2}\nabla_x^2 + (k-1)e^{-(x-X_A)^2} - ke^{-(x-X_B)^2}, \quad (14)$$

with respect to the field parameter $k \in [0, 1]$, shifting the Gaussian potential centered at X_A ($k=0$) to the same potential, but centered at X_B ($k=1$). The figure shows the corresponding change in the density. The average absolute energy error for $k \in [0, 1]$ and the two-norm error of the

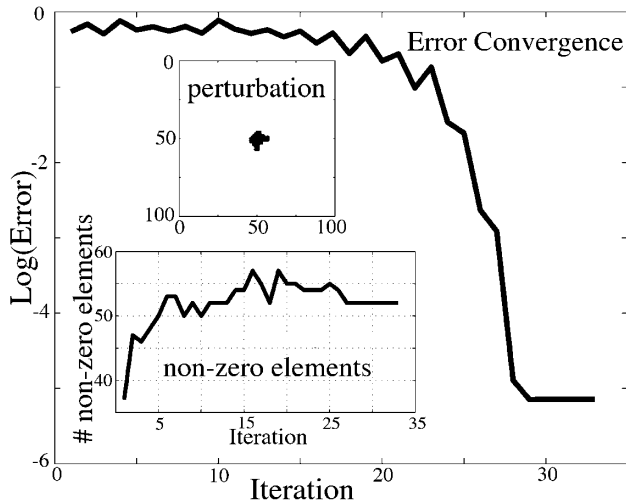


FIG. 1. The $\text{Log}(\text{Error}) = \log_{10}(\|X_n^{(0)} + \Delta_n - P_{\text{exact}}\|_2)$ as a function of iterations n ($N = 100$; $N_e = 50$). The lower inset shows the number of nonzero matrix elements of Δ_n above the threshold $\tau = 10^{-6}$. The upper inset shows the nonzero matrix elements in the perturbation Δ_n at convergence.

density matrix response at $k = 1$, using Eqs. (10) and (12) or (13), decay exponentially with expansion order, as shown in the upper inset. Note the grand canonical perturbation theory works effortlessly even up to 11th order in energy (10th order in density) for this example, since no states cross the chemical potential for $k \in [0, 1]$. For nonmetals with a band gap, and for fairly weak perturbations, this is generally the case and the theory should apply. An extension to *ab initio* calculations is given in a future publication [22], and a more detailed analysis of convergence will be given elsewhere.

The present formulation has been developed in an orthogonal representation. With an N -scaling congruence transformation [24,25], it is straightforward to employ this representation when using a nonorthogonal basis. A change in the inverse overlap matrix S^{-1} due to a local perturbation dS is given by the recursion,

$$\delta_{n+1} = (S_0^{-1} + \delta_n)dS(S_0^{-1} + \delta_n) - \delta_n S_0 \delta_n, \quad (15)$$

where $S = S_0 - dS$, $\delta_0 = 0$, and $S^{-1} = S_0^{-1} + \lim_{n \rightarrow \infty} \delta_n$. The equation contains terms only with local sparse updates and the computational cost scales linearly, $O(N_{\text{pert}})$, with the size of the perturbed region. Similar schemes for the sparse inverse Cholesky or square root factorizations can also be used [26].

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 Δ_n and the problem can be avoided, for example, the single particle energy change $\Delta E = \lim_{n \rightarrow \infty} \text{Tr}(H\Delta_n)$. Connecting and disconnecting individual weakly interacting quantum subsystems can be performed by treating off-diagonal elements of the

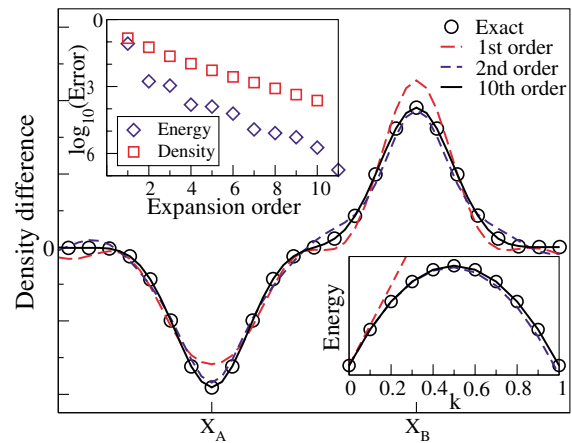


FIG. 2 (color online). The change in density for the Hamiltonian given in Eq. (14) for $k \in [0, 1]$. The boundary conditions are periodic and $N_e = 5$.

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 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 [22], impurities, effective medium, and local scattering techniques [4,5,27,28]. The grand canonical density matrix perturbation theory is thus a rich field with applications in many areas of materials science, chemistry, and biology.

In summary, we have introduced an orbital-free grand canonical perturbation theory for the zero temperature density matrix, extending quadratically convergent purification techniques to expansions of the density matrix upon variation 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 Fig. 1. A quadratically convergent N -scaling recursive approach to computing density matrix response functions was proposed, and energy expressions to 4th order in terms of only first and second order density matrix response were given. The proposed quantum perturbation theory is surprisingly simple and offers an efficient alternative to several Green’s function or wave function methods and conventional schemes for solution of the coupled-perturbed self-consistent-field equations.

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 [17] The notation: θ is the Heaviside step function, μ is the chemical potential, $I = \delta(\mathbf{r}-\mathbf{r}')$, $H = H(\mathbf{r}, \mathbf{r}')$, $P = P(\mathbf{r}, \mathbf{r}')$, $\text{Tr}(A) = \int d\mathbf{r} A(\mathbf{r}, \mathbf{r})$, $AB = \int d\mathbf{r}'' A(\mathbf{r}, \mathbf{r}'') B(\mathbf{r}'', \mathbf{r}')$, the density $n(\mathbf{r}) = P(\mathbf{r}, \mathbf{r})$, the single particle energy $E = \text{Tr}(HP)$, N_e is the number of occupied states below μ , and N is the total number of states corresponding to the system size. For the projections in Eq. (3) $\beta = H_{\text{max}}$ and $\alpha = (H_{\text{max}} - H_{\text{min}})^{-1}$, where H_{max} (H_{min}) are estimates of the spectral bound of H . The anticommutator $\{A, B\} = AB + BA$ and the commutator $[A, B] = AB - BA$.
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