Canonical density matrix perturbation theory

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Abstract

Density matrix perturbation theory [Niklasson and Challacombe, Phys. Rev. Lett. 92, 193001 (2004)] is generalized to canonical (NVT) free energy ensembles in tight-binding, Hartree-Fock or Kohn-Sham density functional theory. The canonical density matrix perturbation theory can be used to calculate temperature dependent response properties from the coupled perturbed self-consistent field equations as in density functional perturbation theory. The method is well suited to take advantage of sparse matrix algebra to achieve linear scaling complexity in the computational cost as a function of system size for sufficiently large non-metallic materials and metals at high temperatures.

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I. INTRODUCTION

Materials properties such as electric conductivity, magnetic susceptibility or electrical polarizabilities, are defined from their response to perturbations that are governed by the quantum nature of the electrons. The calculation of such quantum response properties represents a major challenge because of the high cost involved. In regular calculations the computational complexity scales cubically, $O(N^3)$, or worse, with the number of atoms $N$, even when effective mean field models or density functional theory are used [1, 2]. By using the locality of the electronic solutions it is possible to reduce the computational cost for sufficiently large, non-metallic, materials to scale only linearly, $O(N)$, with the system size [3–10]. Initially, the development of linear scaling electronic structure theory was aimed at calculating ground state properties and not until recently has the focus shifted towards the computationally more demanding task of calculating the quantum response. A number of approaches to a quantum perturbation theory with reduced complexity have now been proposed and analyzed [11–22]. Linear scaling quantum perturbation theory has so far mainly concerned properties at zero electronic temperature. Here we extend the idea behind linear scaling density matrix perturbation theory [16–19] to calculations of static response properties valid also at finite electronic temperatures. Our proposed canonical density matrix perturbation theory, which is applicable within effective single-particle formulations, such as tight-binding, Hartree-Fock or Kohn-Sham density functional theory, can be applied to calculate temperature dependent response properties from the solution of the coupled perturbed self-consistent field equations [1, 23, 24] as in density functional perturbation theory [2, 25]. While originally motivated by its ability to achieve linear scaling complexity, our canonical density matrix perturbation theory is quite general and straightforward to use with high efficiency also for material systems that are too small to reach the linear scaling regime. The canonical density matrix perturbation scheme should be applicable in a number of existing program packages for linear scaling electronic structure calculations, including CONQUEST [9, 26, 27], LATTE [28, 29], FEMTECK [30, 31], FreeON [32], CP2K [33], HONPAS [34], ERGO [35, 36], OPEN-MX [37], ONETEP [38], and SIESTA [39].

The paper is outlined as follows; first we present the canonical density matrix perturbation theory. Thereafter we show how it can be used to calculate temperature dependent free energy response properties, such as static polarizabilities and hyperpolarizabilities. We
discuss the alternative of using finite difference schemes and its potential problems. We conclude by discussing the capability of the canonical density matrix perturbation theory to reach linear scaling complexity in the computational cost.

II. CANONICAL DENSITY MATRIX PERTURBATION THEORY

In our density matrix perturbation theory we will use the single-particle density matrix and its derivatives to represent the electronic structure and its response to perturbations. With the density matrix formulation it is easy to utilize matrix sparsity from electronic nearsightedness \[6, 18, 40, 41\] and it allows direct calculations of observables. The effective single-particle density matrix, \( P \), at the electronic temperature \( T_e \), can be calculated from the Hamiltonian, \( H \), using a recursive Fermi operator expansion \[42–45\],

\[
P = \left[ e^{\beta(H-\mu I)} + 1 \right]^{-1}
\]

\[
\approx \mathcal{F}_M(\mathcal{F}_{M-1}(\ldots \mathcal{F}_0(H) \ldots)),
\]

where the inverse temperature \( \beta = 1/(k_B T_e) \), \( \mu \) is the chemical potential and \( I \) is the identity matrix. Both \( H \) and \( P \) are here assumed to be matrix representations in an orthogonal basis. The expansion can be calculated through intermediate matrices \( X_n = \mathcal{F}_n(X_{n-1}) \) for \( n = 1, 2, 3, \ldots, M \), where

\[
X_0 = \mathcal{F}_0(H) = 0.5I - 2^{-(M+2)} \beta(H - \mu I),
\]

\[
X_n = \mathcal{F}_n(X_{n-1}) = \frac{X_{n-1}^2}{X_{n-1}^2 + (I - X_{n-1})^2}.
\]

In the canonical (NVT) ensemble, the chemical potential \( \mu \) is chosen such that the density matrix has the correct occupation, \( Tr[P] = N_{occ} \), where \( N_{occ} \) is the number of occupied states. The recursion scheme above provides a very efficient and rapidly converging expansion and the number of recursion steps \( M \) can be kept low (\( M < 20 \)). Because of the particular form of the Padé polynomial \( \mathcal{F}_n(X_{n-1}) \), each iteration involves a solution of a system of linear equations, which is well tailored for the linear conjugate gradient method \[42, 43\]. The recursive expansion avoids the calculation of individual eigenvalues and eigenfunctions and is therefore well suited to reach linear scaling complexity in the computational
cost for sufficiently large non-metallic problems, which can utilize thresholded sparse matrix algebra \[6\].

A canonical density matrix response expansion,

\[ P(\lambda) = P^{(0)} + \lambda P^{(1)} + \lambda^2 P^{(2)} + \ldots, \]  

where \( Tr[P^{(k)}] = 0 \) for \( k > 0 \), with respect to a perturbation in the Hamiltonian,

\[ H(\lambda) = H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} + \ldots, \]  

can be constructed at finite electronic temperatures, \( T_e > 0 \), based on the recursive Fermi operator expansion in Eqs. \[1\] and \[2\] above. The technique is given by a free energy generalization of the zero temperature linear scaling density matrix perturbation theory \[16, 17\]. The idea is to transfer the perturbations up to some specific order in each iteration step in the recursive Fermi-operator expansion, i.e.

\[ X_{n}^{(k)} = \left. \frac{1}{k!} \frac{\partial^k}{\partial \lambda^k} F_n(X_{n-1}^{(0)} + \lambda X_{n-1}^{(1)} + \ldots) \right|_{\lambda=0}, \]  

for \( n = 0, 1, \ldots, M \), where \( X_{-1}^{(k)} = H^{(k)} \). The additional problem of conserving the number of particles in a canonical ensemble, which requires \( Tr[P^{(k)}] = 0 \) for \( k > 0 \), is achieved by including the corresponding perturbative expansion of the chemical potential, i.e.

\[ \mu = \mu(\lambda) = \mu^{(0)} + \lambda \mu^{(1)} + \lambda^2 \mu^{(2)} + \ldots. \]  

The values of \( \mu^{(k)} (k = 0, 1, 2, \ldots) \) can be found by an iterative Newton-Raphson optimization of the occupation error with respect to the chemical potential using the relation

\[ P_\mu = \left. \left( \frac{1}{\lambda^k} \frac{\partial P}{\partial \mu^{(k)}} \right) \right|_{\lambda=0} = \beta P^{(0)}(I - P^{(0)}), \]  

which for the approximate expanded density matrix, Eqs. \[1\] and \[2\], is exact in the limit \( M \to \infty \).

The canonical density matrix perturbation theory based on Eqs. \[1-7\] above, which is our first key result, is summarized by Algorithm \[1\] for up to third order response. Each inner loop requires the solution of a system of linear equations, which can be achieved with the conjugate gradient method using \( X_{n-1}^{(k)} \) as initial guesses. The linear conjugate gradient method \[46\] is ideal for this purpose, since it efficiently can take advantage of matrix sparsity to reduce the scaling of the computational cost \[42\]. Generalizations and modifications to higher order response, grand canonical schemes (with a fixed value of \( \mu \)), or spin-polarized (unrestricted) systems are straightforward.
Algorithm 1: Canonical density matrix response theory

\[ M \leftarrow \text{Number of recursion steps} \]
\[ \mu^{(0)} \leftarrow \text{Initial guess} \]
\[ \mu^{(i)} \leftarrow 0 \text{ Initial guess } \{i = 1, 2, 3\} \]
\[ \beta = 1 / (k_B T_e) \leftarrow \text{Choose temperature} \]

\[ \text{while Occupation error } > \text{Tolerance do} \]
\[ X_0^{(0)} = \frac{1}{2} I - 2^{-2+M} \beta (H^{(0)} - \mu^{(0)} I) \]
\[ X_0^{(i)} = -2^{-2+M} \beta (H^{(i)} - \mu^{(i)} I), \{i = 1, 2, 3\} \]

\[ \text{for } n = 1 : M \text{ do} \]
\[ \text{solve for } X_n^{(i)}, \{i = 0, 1, 2, 3\} \]
\[ T_{n-1}^{(0)} X_n^{(0)} = C_n^{(0)} \]
\[ T_{n-1}^{(0)} X_n^{(1)} = C_n^{(1)} + B_{n-1}^{(1)} X_n^{(0)} \]
\[ T_{n-1}^{(0)} X_n^{(2)} = C_n^{(2)} + B_{n-1}^{(2)} X_n^{(0)} + B_{n-1}^{(1)} X_n^{(1)} \]
\[ T_{n-1}^{(0)} X_n^{(3)} = C_n^{(3)} + B_{n-1}^{(3)} X_n^{(0)} + B_{n-1}^{(2)} X_n^{(1)} + B_{n-1}^{(1)} X_n^{(2)} \]
\[ \text{end for} \]
\[ P^{(i)} = X_M^{(i)}, \{i = 0, 1, 2, 3\} \]
\[ \mu^{(0)} = \mu^{(0)} + (N_e - \text{Tr}[P^{(0)}]) / \text{Tr}[P^{(0)}] \]
\[ \mu^{(i)} = \mu^{(i)} - \text{Tr}[P^{(i)}] / \text{Tr}[P^{(0)}], \{i = 1, 2, 3\} \]

\[ \text{Occupation error } = \sum_{i=0}^{3} |\text{Tr}[P^{(i)}] - N_e| \]
\[ \text{end while} \]

using:
\[ P_\mu = \beta P^{(0)} (I - P^{(0)}) \]
\[ T_n^{(0)} = 2 X_n^{(0)} (X_n^{(0)} - I) + I \]
\[ C_n^{(M)} = \sum_{i+j=M} X_n^{(i)} X_n^{(j)}, \{i, j \geq 0\} \]
\[ B_n^{(M)} = 2 (X_n^{(M)} - C_n^{(M)}) \]

III. FREE ENERGY RESPONSE THEORY

To study the quantum response valid at finite electronic temperatures, the electronic entropy contribution to the free energy has to be considered. In a simple tight-binding like
formulation, the expansion terms for the canonical free energy,
\[ \Omega(\lambda) = Tr[P(\lambda)H(\lambda)] - T_e S[P(\lambda)] = \]
\[ = \Omega^{(0)} + \lambda \Omega^{(1)} + \lambda^2 \Omega^{(2)} + \ldots, \]
generated by a perturbation in \( H(\lambda) \), Eq. (4), with the electronic entropy \[43, 47\],
\[ S[P] = -k_B Tr[P \ln(P) + (I - P) \ln(I - P)], \]
are given by
\[ \Omega^{(m)} = \frac{1}{m} \sum_{k=1}^{m} k Tr[H^{(k)} P^{(m-k)}]. \]
This expression, with \( P^{(k)} \) calculated from our canonical density matrix perturbation scheme in Algorithm 1, is a straightforward generalization of the conventional \( T_e = 0 \) limit of the “\( n + 1 \)” rule \[19\]. This generalization is possible only by including the entropy term in Eq. (8), which is required to provide a variationally correct description of the energetics. We have not been able to find any explicit density matrix expressions for Wigner’s \( 2n + 1 \) rule \[16, 18, 48–52\] that are valid also at finite temperatures.

A. Self-consistent free energy response

In self-consistent first principles approaches such as Hartree-Fock theory \[53\] (density functional and self-consistent tight-binding theory, although different, follow equivalently) the free energy in the restricted case (without spin polarization) is given by a constrained minimization of the functional
\[ \Omega_{\text{SCF}}[D] = 2Tr[hD] + Tr[DG(D)] - 2T_e S[D^\perp], \]
under the condition that \( 2Tr[DS] = N_e \), where \( N_e \) is the number of electrons (two in each occupied state). Here \( D^\perp \) is the orthogonalized representation of the Hartree-Fock density matrix \( D \) such that \( D = Z D^\perp Z^T \), and the orthogonalized effective single-particle Hamiltonian is given by \( F^\perp = Z^T F Z \), where the Fockian \( F = h + G(D) \) and \( Z \) is the inverse factor of the basis set overlap matrix \( S \) such that \( Z^T S Z = I \). The density matrix, \( D \), is thus given by
\[ D = Z \left[ e^{\beta(F^\perp - \mu I)} + 1 \right]^{-1} Z^T, \]
which can be calculated through the recursive Fermi operator expansion in Eqs. (1) and (2). Here \( h \) is the usual one-electron term and \( G(D) \) is the conventional two-electron part including the Coulomb \( J \) and exchange term \( K \), respectively [53]. In density functional theory, the Fockian \( F \) is replaced by the corresponding Kohn-Sham Hamiltonian, where the exchange term \( K \) is substituted with the exchange-correlation potential term.

With a basis-set independent first order perturbation in the one-electron term,

\[
h(\lambda) = h(0) + \lambda h^{(1)},
\]

(13)

for example due to an external electric field, the self-consistent response in the density matrix is given by the solution of the coupled perturbed self-consistent-field (SCF) equations as in density functional perturbation theory:

\[
F(\lambda) = h(0) + \lambda h^{(1)} + G(D(0) + \lambda D^{(1)} + \ldots),
\]

\[
F^\perp(\lambda) = Z^T F(\lambda) Z,
\]

(14)

\[
D(\lambda) = Z \left[ e^{\beta(F^\perp(\lambda) - \mu I)} + 1 \right]^{-1} Z^T,
\]

where \( D \) and \( F \) are expanded in terms of \( \lambda \), i.e.

\[
D(\lambda) = D(0) + \lambda D^{(1)} + \lambda^2 D^{(2)} + \ldots,
\]

(15)

\[
F(\lambda) = F(0) + \lambda F^{(1)} + \lambda^2 F^{(2)} + \ldots.
\]

The coupled response equations above are solved in each iteration using the canonical density matrix perturbation theory as implemented in Algorithm 1 with \( H \) and \( P \) replaced by \( F \) and \( D \). At self consistency, the free energy expansion terms,

\[
\Omega_{SCF}(\lambda) = \Omega_{SCF}[D(0)] + \lambda \Omega_{SCF}^{(1)} + \lambda^2 \Omega_{SCF}^{(2)} + \ldots
\]

(16)

are given by

\[
\Omega_{SCF}^{(m)} = \frac{2}{m} Tr[h^{(1)} D^{(m-1)}] \quad m > 0.
\]

(17)

This simple and convenient expression for the basis-set independent free energy response, which follows from Eq. (10), is another key result of this paper. The free energy response theory presented here provides a general technique to perform reduced complexity calculations, of for example, temperature-dependent static polarizabilities and hyperpolarizabilities [17, 18].
IV. FINITE DIFFERENCE APPROXIMATIONS

An alternative to the canonical density matrix perturbation theory is to perform calculations with finite perturbations and use finite difference approximations of the free energy derivatives. However, this can be far from trivial because the numerical errors are sometimes difficult to estimate and control, in particular for high temperature hyperpolarizabilities. Nevertheless, by using finite steps $\delta\lambda$ of the perturbations in $\hbar$, combined with multi-point high-order finite difference schemes, it is sometimes possible to reach good accuracy. This is illustrated in Fig. 1 which shows the finite difference error in the approximation of the second order free energy response, $\Omega_{\text{SCP}}^{(2)}$, with respect to an external electric field for a self-consistent tight-binding model [54–57] as implemented in the electronic structure program package LATTE [28, 29]. Finite difference calculations of higher-order hyperpolarizabilities show similar behavior.

In a finite difference approximation it is difficult to know a priori what step size $\Delta\lambda$ to use for the perturbations $\lambda h^{(1)}$ in Eq. (13). Errors may be large unless a careful numerical testing is performed. This can be expensive and even when an accurate step size has been found, the computational cost is still higher compared to the analytical approach. For example, to calculate the second order response using the five point finite difference scheme has a computational cost of about 5 times a ground state calculation, whereas the cost for the density matrix perturbation theory is only about 3 times larger. This cost estimate does not include the additional entropy calculations. The calculation of the entropy is difficult (or impossible) to perform accurately within linear scaling complexity. Computationally favorable formulations that are based on approximate expansions of $S[P]$ in Eq. (9) are typically poor. For example, when any of the approximate entropy expressions,

$$S_m[P] \approx -k_B \sum_{i=1}^{m} c_i(m) Tr[P^m (P - I)^m],$$

(18)

with the coefficients $c_i(m)$ in Tab. 1 are used, the relative error of the polarizability in Fig. 1 is increased by over 6 orders of magnitude for the most accurate 9 point finite difference approximation. The accuracy is at best only about 0.5 percent with any of the entropy approximations in Eq. (18) and Tab. 1. Only by avoiding explicit entropy calculations it is possible to reach a meaningful accuracy. This is possible in a finite difference approximation by using the finite differences of the dipole moments instead of the free energies. Such
FIG. 1: The relative error compared to the “exact” derivative in Eq. (17) for $\Omega_{SCF}^{(2)}$ using 5 and 9 point central difference schemes for the calculation of the second order response in the free energy with respect to an external electric field, i.e. the polarizability. Either the exact entropy expression was used, Eq. (9), or the highest order $(m = 4)$ approximation in Eq. (18). The electronic temperature $T_e$ is about 37,000 K.

TABLE I: Coefficients for the approximate entropy expression in Eq. (18). The coefficients are determined from the ansatz in Eq. (18) with the requirement that the function value and a few of its derivatives are correct at the midpoint 0.5 of the interval [0,1] in which $P$ has its eigenvalues.

| $c_i(m)$ | $m = 1$ | $m = 2$ | $m = 4$ |
|---------|---------|---------|---------|
| $c_1(m)$ | $4 \ln(2)$ | $8 \ln(2) - 2$ | $16 \ln(2) - 34/5$ |
| $c_2(m)$ | $16 \ln(2) - 8$ | $96 \ln(2) - 844/15$ |
| $c_3(m)$ | | $256 \ln(2) - 2336/15$ |
| $c_4(m)$ | | $256 \ln(2) - 2368/15$ |

calculations (not shown) avoids calculating the explicit entropy term and the numerical accuracy is similar to the finite difference approximations using the free energies with the exact entropy expression as illustrated in Fig. 1.
FIG. 2: (color online) The isotropic temperature dependent response \( \Omega_{\text{SCF}}^{(m)} = \frac{1}{3}(\Omega_{\text{SCF}(xx)}^{(m)} + \Omega_{\text{SCF}(yy)}^{(m)} + \Omega_{\text{SCF}(zz)}^{(m)}) \) for a single water molecule. At low temperatures the response corresponds to regular polarizabilities and hyperpolarizabilities (rescaled by \( m! \)).

V. FIRST PRINCIPLES RESULTS

A. Polarizabilities and hyperpolarizabilities

Figure 2 shows the calculated temperature-dependent response for a single water molecule with respect to a frequency-independent electric field. The calculations were performed with Hartree-Fock theory using the ERGO program package [35, 36]. At lower temperatures the isotropic response values correspond to the polarizabilities and hyperpolarizabilities. At higher temperatures this interpretation is less accurate because of the limited basis set description of the thermally excited states. For relevant temperatures below 10,000 K our calculations shows a very small temperature dependence, which is consistent with a fairly large HOMO-LUMO gap. The calculations were performed for a single molecule in the gas phase. For periodic boundary conditions the position and the dipole moment operator are not well defined. In this case the techniques developed within the modern theory of polarizability can be applied [58, 61].

B. Linear scaling complexity

It is easy to understand the linear scaling capability of canonical density matrix perturbation theory. Thanks to nearsightedness [6, 18, 40, 41], both the Hamiltonian and its
perturbations, as well as the density matrix and its response, have sparse matrix representations for non-metallic materials when local basis set representations are used. The number of significant matrix elements above some small numerical threshold then scales only linearly with the number of atoms for sufficiently large systems. In this case, since all operations in the canonical density matrix perturbation scheme in Algorithm 1 are based on matrix-matrix operations, the computational cost scales only linearly with system size if sparse matrix algebra is used in the calculations. This is not possible in regular Rayleigh-Schrödinger perturbation theory, which requires the calculation of individual eigenvalues and eigenfunctions. Figure 3 shows the number of non-zero elements above threshold as a function of system size for the density matrix and its first and second order response with respect to an electric dipole perturbation. The test systems are simple one-dimensional hydrocarbon chains of various lengths. The calculations where performed based on Hartree-Fock theory and a simple Gaussian (STO-3G) basis. At higher temperatures the locality, i.e. the matrix sparsity, is increased similar to what is found for larger HOMO-LUMO gaps [6], and for higher order response the locality decreases, as has been seen in previous studies for the zero temperature case [17] [18].
VI. SUMMARY

In summary, we have presented a canonical single-particle density matrix perturbation scheme that enables the calculation of temperature dependent quantum response properties. Since our approach avoids the calculation of individual eigenvalues and eigenfunctions as well as the entropy, the theory is well adapted for reduced complexity calculations with a computational effort that scales only linearly with the system size. The perturbation scheme should be applicable in a number of existing program packages for linear scaling electronic structure calculations.

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