Ab Initio Linear Scaling Response Theory: Electric Polarizability by Perturbed Projection

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A linear scaling method for calculation of the static *ab initio* response within self-consistent field theory is developed and applied to the calculation of the static electric polarizability. The method is based on the density matrix perturbation theory [Niklasson and Challacombe, preceding Letter, Phys. Rev. Lett. **92**, 193001 (2004)], obtaining response functions directly via a perturbative approach to spectral projection. The accuracy and efficiency of the linear scaling method is demonstrated for a series of three-dimensional water clusters at the RHF/6-31G** level of theory. The locality of the response under a global electric field perturbation is numerically demonstrated by the approximate exponential decay of derivative density matrix elements.

Linear scaling methods that reduce the computational complexity of electronic structure calculations to $O(N)$, where N is system size, impact disciplines that demand quantum simulation of increasingly large and complex systems [1]. To date, the most successful and prolific applications of linear scaling technologies are ground state studies involving empirical model Hamiltonians. To a lesser degree, ground state applications using *ab initio* models with N scaling contribute to a variety of fields, typically at the self-consistent-field (SCF) level of theory and requiring in some cases parallel implementations to reach levels of applicability comparable with empirical models. These SCF theories include the Hartree-Fock (HF), Kohn-Sham density functional (DF) and hybrid HF-DF models.

Beyond ground state methods, little attention has been given to linear scaling algorithms for the computation of dynamic and static response properties, the latter including the nuclear magnetic shielding tensor [2], the rotational g-tensor [3], indirect spin-spin coupling constant [4], third order properties such as the first hyperpolarizability [5], and polarizability derivatives such as the Raman intensity [6]. Dynamic properties may be computed using linear scaling algorithms to propagate the density matrix [7,8] in the time domain, followed by convolution to obtain the spectral response. In this way, Yam, Yokojima, and Chen [8] have recently demonstrated linear scaling computation of the absorption spectra for one-dimensional polymers at the local density level of theory, but requiring $\sim 14\,000$ time steps. In the static zero frequency limit, solving the coupled-perturbed self-consistent-field (CPSCF) equations using standard algorithms is likewise difficult for large systems. Several algorithms have therefore been proposed for solving the CPSCF equations that may be capable of achieving a reduced scaling better than $O(N^3)$ [9,10].

In this Letter, we develop the density matrix perturbation theory of Niklasson and Challacombe [11] for the N-scaling solution of the *ab initio* CPSCF equations and demonstrate the early onset of linear scaling for the accurate calculation of the first electric polarizability of three-dimensional systems using large basis sets. This perturbed projection method is general and can be extended to a variety of static properties.

Algorithms for linear scaling SCF theory exploit the quantum locality of nonmetallic systems, manifested in the approximate exponential decay of the density matrix with atom-atom separation, through the effective use of sparse matrix methods and iterative approaches to spectral projection [12,13]. This quantum locality should, in principle, extend also to the derivative density matrices central to the CPSCF equations. Indeed, exponential decay of the derivative density matrix within *ab initio* SCF theory has been demonstrated numerically for local nuclear displacement [14]. However, standard approaches to the CPSCF equations [15] do not admit exploitation of this locality, as they are based on perturbation of the wave function, requiring $O(N^3)$ eigensolution and typically $O(N^5)$ transformation of two-electron integrals into the eigenbasis. Avoiding both eigensolution and integral transformation, Ochsenfeld and Head-Gordon [14] and later Larsen *et al.* [16] proposed iterative solutions to the CPSCF equations involving purely nonorthogonal representations. In both of these approaches, a linear system of equations containing commutation relations must be solved.

Recently, a formulation of density matrix perturbation theory has been proposed by Niklasson and Challacombe (NC) [11] that presents a new opportunity for solving the CPSCF equations within the context of linear scaling spectral projection [12,13]. The new approach is based on the relationship between the density matrix $\mathcal{D}$ and the effective Hamiltonian or Fockian $\mathcal{F}$ through the spectral projector (Heaviside step function) $\mathcal{D} = \theta(\tilde{\mu}I - \mathcal{F})$, where the chemical potential $\tilde{\mu}$ determines the occupied states via Aufbau filling. Spectral projection can be carried out in a number of ways [12,13,17]. Recently, new recursive polynomial expansions of the projector have

emerged, such as the second order trace correcting (TC2) [12] and fourth order trace resetting (TRS4) [13] purification. These new methods (TC2 and TRS4) have convergence properties that depend only weakly on the band gap, do not require knowledge of the chemical potential, and perform well for all occupation to state ratios. In the NC approach, the perturbation expansion is developed within the reference ground state projector allowing order by order collection of terms at each iteration, establishing a quadratically convergent sequence for the response functions.

In the following, the indexes $a, b, \ldots$ refer to perturbation order, while $i, j, \ldots$ mark the iteration count. The symbols $\mathcal{D}, \mathcal{F}, \ldots$ are matrices in an orthogonal representation, while $D, F, \ldots$ are the corresponding matrices in a nonorthogonal basis. The transformation between orthogonal and nonorthogonal representations is carried out in $O(N)$ using congruence transformations [18] provided by the AINV algorithm for computing sparse approximate inverse Cholesky factors [19].

Within HF theory, the total electronic energy E_{tot} of a molecule in a static electric field $\mathcal{E}$ is

$$E_{\text{tot}}(\mathcal{E}) = \text{Tr}[D(h^0 + \mu\mathcal{E})] + \tfrac{1}{2}\text{Tr}\{D[J(D) + K(D)]\}, \quad (1)$$

where D is the density matrix in the electric field, h^0 is the core Hamiltonian, μ is the dipole moment matrix, $J(D)$ is the Coulomb matrix, and $K(D)$ is the exact HF exchange matrix. The total energy may be developed in the perturbation expansion

$$E_{\text{tot}}(\mathcal{E}) = E_{\text{tot}}(0) - \sum_a \mu_a \mathcal{E}^a - \frac{1}{2}\sum_{ab} \alpha_{ab}\mathcal{E}^a\mathcal{E}^b + \ldots, \quad (2)$$

where α_{ab} is the first order polarizability, μ_a is the dipole moment, and $\mathcal{E}^a$ is the electric field in direction a. The polarizability is the second order response of the total energy with respect to variation in the electric field [15]

$$\alpha_{ab} = -\frac{\partial^2 E_{\text{tot}}}{\partial\mathcal{E}^a \partial\mathcal{E}^b}\bigg|_{\mathcal{E}=0} = -2\text{Tr}[D^a\mu_b]. \quad (3)$$

The first order density matrix derivative $\mathcal{D}^a$ in the a direction is obtained by variation of both the spectral projector θ and the Fockian $\mathcal{F} = \mathcal{F}^0 + \sum_a \mathcal{E}^a \mathcal{F}^a + \cdots$ as

$$\mathcal{D}^a = \frac{\partial}{\partial\mathcal{E}^a}\theta(\tilde{\mu}I - (\mathcal{F}^0 + \mathcal{E}^a\mathcal{F}^a))\bigg|_{\mathcal{E}=0}. \quad (4)$$

The HF Fockian F^0 in the nonorthogonal basis is $F^0 = h^0 + J(D^0) + K(D^0)$, where the Coulomb matrix J may be computed in $O(N\lg N)$ with a quantum chemical tree code (QCTC) [20] and the exchange matrix K computed in $O(N)$ with the ONX algorithm that exploits quantum locality of D^0 [21]. Likewise the derivative Fockian, $F^a = \mu_a + J(D^a) + K(D^a)$, may be computed with the same algorithms in linear scaling time if D^a manifests decay properties similar to D^0. A similar equation holds

for the derivative Fockian within DF and hybrid HF-DF theories with the addition of the exchange-correlation matrix $V^a_{xc}(D^0, D^a)$ [22].

In our approach to linear scaling computation of the polarizability α_{ab}, the ground state density matrix $\mathcal{D}^0$ is computed using a spectral projection algorithm such as TC2 [12] in conjunction with sparse atom-blocked linear algebra [13,23]. Linear scaling is achieved for insulating systems through the dropping (filtering) of atom-atom blocks with the Frobenious norm below a numerical threshold ($\sim 10^{-4}$–10^{-6}). At SCF convergence the TC2 algorithm generates a polynomial sequence defining the ground state projector, from which expansion of the derivative density matrix can be obtained term by term.

The derivative density matrix and derivative Fockian depend on each other implicitly and must be solved for self-consistently via the CPSCF equations. The necessary and sufficient criteria for convergence of the CPSCF equations are $[\mathcal{F}^a, \mathcal{D}^0] + [\mathcal{F}^0, \mathcal{D}^a] = 0$ and $\mathcal{D}^a = \mathcal{D}^a\mathcal{D}^0 + \mathcal{D}^0\mathcal{D}^a$ [24]. Solution of the CPSCF equations with perturbed projection involves the steps

$$F^a_n = \mu_a + J(D^a_n) + K(D^a_n), \quad (5a)$$

$$\tilde{F}^a_n = \sum_{k=n-m}^{n} c_k F^a_k, \quad (5b)$$

$$\mathcal{D}^a_{n+1} = \frac{\partial}{\partial\mathcal{E}^a}\theta(\tilde{\mu}I - (\mathcal{F}^0 + \mathcal{E}^a\tilde{\mathcal{F}}^a_n))\bigg|_{\mathcal{E}=0} \quad (5c)$$

with starting point $D^a_0 = 0$. In step (5a), F^a_n is constructed in $O(N)$ using the QCTC [20] and ONX [21] algorithms in MONDOSCF [25]. Next, Weber and Daul's DDIIS algorithm for convergence acceleration of the CPSCF equations [26] is used to optimize the c_k coefficients in step (5b), keeping the last m steps in the extrapolation. Then, the density matrix derivative $\mathcal{D}^a_{n+1}$ is obtained in step (5c) as $\mathcal{D}^a_{n+1} = \lim_{i\to\infty}\mathcal{X}^a_i$ via the NC density matrix perturbation theory, based on the TC2 projector:

$$\left.\begin{array}{l}\mathcal{X}^a_{i+1} = \mathcal{X}^a_i\mathcal{X}^0_i + \mathcal{X}^0_i\mathcal{X}^a_i \\ \mathcal{X}^0_{i+1} = (\mathcal{X}^0_i)^2\end{array}\right\} \quad \text{Tr}[\mathcal{X}^0_i] \geq N_e \quad (6)$$

or

$$\left.\begin{array}{l}\mathcal{X}^a_{i+1} = 2\mathcal{X}^a_i - \mathcal{X}^a_i\mathcal{X}^0_i - \mathcal{X}^0_i\mathcal{X}^a_i \\ \mathcal{X}^0_{i+1} = 2\mathcal{X}^0_i - (\mathcal{X}^0_i)^2\end{array}\right\} \quad \text{Tr}[\mathcal{X}^0_i] < N_e. \quad (7)$$

The matrices initiating the sequence are obtained from $\mathcal{F}^0$ and $\mathcal{F}^a$ by appropriately compressing their spectrum into the domain of convergence [12] using

$$\mathcal{X}^0_0 = \frac{\mathcal{F}_{\max} - \mathcal{F}^0}{\mathcal{F}_{\max} - \mathcal{F}_{\min}} \quad \text{and} \quad \mathcal{X}^a_0 = \frac{\mathcal{F}^a_n}{\mathcal{F}_{\min} - \mathcal{F}_{\max}}, \quad (8)$$

where $\mathcal{F}_{\min}$ and $\mathcal{F}_{\max}$ are approximate upper and lower bounds to the eigenvalues of $\mathcal{F}^0$.

Recursion of the perturbed projection sequence is stopped when the change $|\mathcal{X}^a_{i+1} - \mathcal{X}^a_i|$ becomes small.
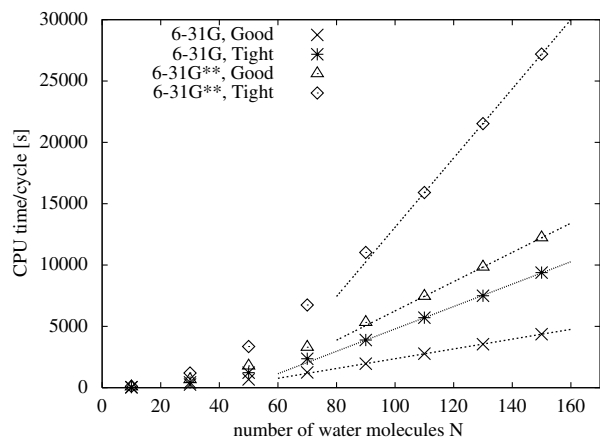
FIG. 1. Total CPU time of the fifth CPSCF iteration for the water cluster sequence with the 6-31G and 6-31G** basis sets and the GOOD and TIGHT numerical thresholds (see text) controlling numerical precision of the result. The lines are fits to the last three and four points, respectively.

Having solved for D_n^a, the next Fock matrix derivative F_{n+1}^a is built, and the iteration continues until self-consistency, when the density matrix derivative D_n^a and the desired property (e.g., the polarizability $\alpha_{ab} = -2\mathrm{Tr}[D_n^a \mu_b]$) have reached a sufficient level of accuracy.

We have implemented these methods in the MONDOSCF suite of linear scaling quantum chemistry programs [25] and performed polarizability calculations on a series of water clusters up to $(H_2O)_{150}$. These clusters were obtained by carving a spherical region out of a snapshot from a periodic classical molecular dynamics simulation of water at standard liquid density and have been used previously in a number of scaling tests [13,20,21].

Calculations have been carried out at both the RHF/6-31G and RHF/6-31G** levels of theory and with both the GOOD and TIGHT thresholding parameter sets that control precision of the linear scaling algorithms, corresponding to matrix thresholds of 10^{-5} and 10^{-6}, respectively. These calculations were carried out on a single Intel Xeon 2.4 GHz processor running RedHat Linux 8.0 and executables compiled with Portland Group Fortran Compiler pgf90 4.0-2 [27]. In Fig. 1, the total CPU time for the fifth CPSCF cycle (including build time for $\mathcal{F}^a$, iterative construction of $\mathcal{D}^a$, and all intermediate steps including congruence transformation) is shown for the RHF/6-31G and RHF/6-31G** series of water clusters. Convergence of the CPSCF equations for these systems is typically achieved in about ten cycles, independent of cluster size, basis set, or matrix threshold. In Table I, the corresponding average water cluster polarizabilities computed with the MONDOSCF algorithms are listed and compared to the those obtained with the GAMESS quantum chemistry package [28] at the RHF/6-31G level of theory. Figure 2 shows the magnitude of density matrix derivative

TABLE I. Average polarizabilities $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3N_{H_2O}$ in a.u. for a sequence of water clusters at the RHF/6-31G and RHF/6-31G** levels of theory.

N_{H_2O}	6-31G[a]	6-31G[b] GOOD	6-31G[b] TIGHT	6-31G**[b] GOOD	6-31G**[b] TIGHT
10	4.569 083	4.569 918	4.569 102	5.479 161	5.479 049
30	4.673 213	4.673 208	4.673 227	5.585 293	5.585 280
50	4.70 3540	4.703 512	4.703 568	5.623 057	5.622 830
70	⋯	4.732 207	4.732 279	5.654 646	5.654 747
90	⋯	4.775 002	4.775 024	5.695 435	5.695 564
110	⋯	4.780 718	4.780 809	5.698 338	5.698 447
130	⋯	4.786 383	4.786 437	5.704 859	5.704 947
150	⋯	4.775 124	4.775 231	5.693 268	5.693 447

[a]GAMESS.
[b]MONDOSCF.

atom-atom blocks as a function of atom-atom distance under global perturbation by a static electric field.

These results demonstrate an onset of linear scaling as early as 70 water molecules for properties with four digits of precision (RHF/6-31G at GOOD). While the CPSCF equations must be solved iteratively with perturbed projection, the number of CPSCF cycles is ~10 when using DDIIS acceleration on well behaved systems.

Using an incomplete sparse linear algebra with thresholding is an advantage of the present implementation, as the small gap limit correctly leads to an $O(N^3)$ algorithm while preserving accuracy. In contrast, methods that employ radial cutoffs incorrectly retain N scaling in this limit at the sacrifice of accuracy. However, the iterative approach proposed here for solution of the CPSCF equations is prone to the same instabilities encountered by the SCF equations in the small gap limit.
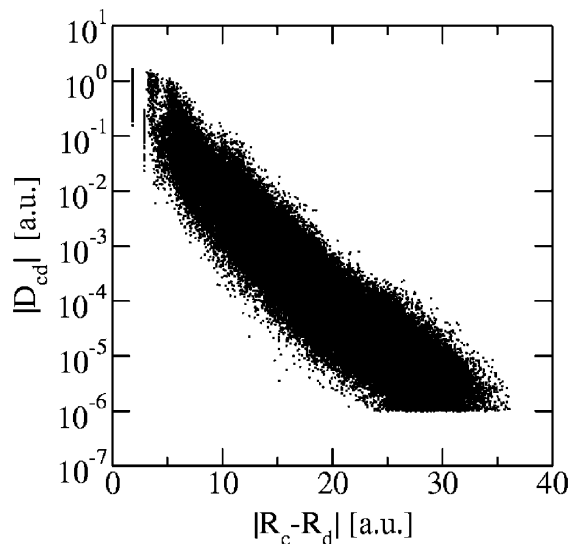

FIG. 2. Magnitudes of atom-atom blocks of the RHF/6-31G density matrix derivative in the z direction with the separation of basis function centers for $(H_2O)_{150}$.

We have shown that the density matrix response is local upon *global* electric perturbation, corresponding to an approximate exponential decay of matrix elements. A similar exponential decay in the first order response corresponding to the *local* nuclear displacement has previously been demonstrated by Ochsenfeld and Head-Gordon [14]. These key observations are expected to hold generally for both local and global perturbations to insulating systems. The implication of these results is that the perturbed projection algorithm described in steps (5a)–(5c) and Eqs. (6) and (7) can be easily extended to the linear scaling computation of higher order response functions, other projections schemes such as TRS4 [13], DF and HF-DF models, and a large class of static molecular properties.

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[1] G. Galli, Curr. Opin. Solid State Mater. Sci. **1**, 864 (1996); D. R. Bowler, M. Aoki, C. M. Goringe, A. P. Horsfield, and D. G. Pettifor, Modell. Simul. Mater. Sci. Eng. **5**, 199 (1997); S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999); P. Ordejon, Phys. Status Solidi B **217**, 335 (2000); V. Gogonea, D. Suarez, A. van der Vaart, and K. W. Merz, Curr Opin Struct Biol **11**, 217 (2001); S. Y. Wu and C. S. Jayanthi, Phys. Rep. **358**, 1 (2002).

[2] K. Wolinski, J. F. Hinton, and P. Pulay, J. Am. Chem. Soc. **112**, 8251 (1990).

[3] J. Gauss, K. Ruud, and T. Helkager, J. Chem. Phys. **105**, 2804 (1996).

[4] C. H. Pennington and C. P. Slichter, Phys. Rev. Lett. **66**, 381 (1991); O. L. Malkina, D. R. Salahub, and V. G. Malkin, J. Chem. Phys. **105**, 8793 (1996).

[5] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, Phys. Rev. Lett. **78**, 3097 (1997).

[6] M. Lazzeri and F. Mauri, Phys. Rev. Lett. **90**, 36401 (2003); O. Quinet and B. Champagne, J. Chem. Phys. **115**, 6293 (2001).

[7] S. Nomura, T. Iitaka, X. W. Zhao, T. Sugano, and Y. Aoyagi, Phys. Rev. B **56**, R4348 (1997).

[8] C. Y. Yam, S. Yokojima, and G. H. Chen, Phys. Rev. B **68**, 153105 (2003).

[9] C. Ochsenfeld and M. Head-Gordon, Chem. Phys. Lett. **270**, 399 (1997).

[10] H. Larsen, T. Helgaker, J. Olsen, and P. Jorgensen, J. Chem. Phys. **115**, 10 344 (2001).

[11] A. M. N. Niklasson and M. Challacombe, preceding Letter, Phys. Rev. Lett., **92**, 193001 (2004).

[12] A. M. N. Niklasson, Phys. Rev. B **66**, 155115 (2002).

[13] A. M. N. Niklasson, C. J. Tymczak, and M. Challacombe, J. Chem. Phys. **118**, 8611 (2003).

[14] C. Ochsenfeld and M. Head-Gordon, Chem. Phys. Lett. **270**, 399 (1997).

[15] J. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem., Quantum Chem. Symp. **S13**, 225 (1979); H. Sekino and R. J. Bartlett, J. Chem. Phys. **85**, 976 (1986); S. P. Karna and M. Dupuis, J. Comput. Chem. **12**, 487 (1991).

[16] H. Larsen, T. Helgaker, J. Olsen, and P. Jorgensen, J. Chem. Phys. **115**, 10 345 (2001).

[17] R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960); W. L. Clinton, A. J. Galli, and L. J. Massa, Phys. Rev. **177**, 7 (1969); A. H. R. Palser and D. E. Manolopoulos, Phys. Rev. B **58**, 12 704 (1998); G. Beylkin, N. Coult, and M. J. Mohlenkamp, J. Comput. Phys. **152**, 32 (1999); K. Nemeth and G. E. Scuseria, J. Chem. Phys. **113**, 6035 (2000); A. Holas, Chem. Phys. Lett. **340**, 552 (2001).

[18] J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon Press, Oxford, 1965); G. W. Stewart, *Introduction to Matrix Computations* (Academic Press, London, 1973).

[19] M. Benzi and C. D. Meyer, SIAM J. Sci. Comput. **16**, 1159 (1995); M. Benzi, C. D. Meyer, and M. Tůma, SIAM J. Sci. Comput. **17**, 1135 (1996); M. Benzi, R. Kouhia, and M. Tuma, Comput. Meth. Appl. Mech. Eng. **190**, 6533 (2001).

[20] M. Challacombe and E. Schwegler, J. Chem. Phys. **106**, 5526 (1997).

[21] E. Schwegler, M. Challacombe, and M. Head-Gordon, J. Chem. Phys. **106**, 9708 (1997).

[22] A. M. Lee and S. M. Colwell, J. Chem. Phys. **101**, 9704 (1994).

[23] M. Challacombe, Comput. Phys. Commun. **128**, 93 (2000).

[24] F. Furche, J. Chem. Phys. **114**, 5982 (2001).

[25] M. Challacombe, E. Schwegler, C. Tymczak, C. K. Gan, K. Nemeth, V. Weber, A. M. N. Niklasson, and G. Henkleman, MONDOSCF v1.0α9, a program suite for massively parallel, linear scaling SCF theory and *ab initio* molecular dynamics, 2001, Los Alamos National Laboratory (LA-CC 01-2), © University of California, http://www.t12.lanl.gov/ mchalla/.

[26] V. Weber and C. Daul, Chem. Phys. Lett. **370**, 99 (2003).

[27] The Portland Group, pgf90 4.0-2, http://www.pgroup.com/, 2002.

[28] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).