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Linear-scaling localized-density-matrix method for the ground and excited states of one-dimensional molecular systems

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Abstract

A linear-scaling localized-density-matrix (LDM) method is developed to evaluate the ground-state reduced single-electron density matrices of one-dimensional molecular systems. The new method may be combined with the existing linear-scaling LDM method for the excited states (Yokojima and Chen, Chem. Phys. Lett. 292 (1998) 379), and thus leads to a linear-scaling calculation method for the properties of both the ground and excited states. The combined method is applied to the polyacetylene oligomers and the linear-scaling of the total computational time is clearly demonstrated. © 1999 Elsevier Science B.V. All rights reserved.

Recently a localized-density-matrix (LDM) method was developed to calculate the excited-state properties of very large electronic systems [1–3]. The LDM method includes explicitly the electron–electron Coulomb interaction and its computational time scales linearly with the system size. It has been applied successfully to evaluate absorption spectra of polyacetylene oligomers containing up to 2000 carbon atoms [1]. It starts with the Hartree–Fock (HF) ground-state single-electron reduced density matrix $\rho^{(0)}$, truncates the reduced density $\rho(t)$, and solves the time-dependent HF (TDHF) equation of motion (EOM) [4]

$$i\hbar \dot{\rho}(t) = \left[h(t) + f(t), \rho(t) \right] \tag{1}$$

for the induced reduced density matrix $\delta\rho(t)$, where $\rho(t) \equiv \rho^{(0)} + \delta\rho(t)$, $h(t)$ is the Fock matrix, and

$f(t)$ represents the interaction between the electrons and external field. It was observed that the relation

$$\left[h^{(0)}, \rho^{(0)} \right] = 0 \tag{2}$$

to be satisfied to yield the physical properties. Otherwise, unphysical results may be obtained, for instance, the gains in the absorption spectrum. The many linear-scaling algorithms have been developed to calculate the electronic ground state [5–26]. However, it is not certain that Eq. (2) is satisfied. In this Letter, we report a consistent linear-scaling computation method for the ground- and excited-state reduced density matrices. This method is based on the linear-scaling LDM method for the excited states. For the excited states, it is exactly the same as the existing LDM reported in Ref. [2]. For the ground state, Eq. (2) is solved for the ground-state reduced density matrix $\rho^{(0)}$ with the proper truncation of the reduced density matrix and its idenpotency condi-

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tion. The computational time of the method is expected to scale linearly with the system size. To illustrate the validity of the method, we calculate the ground-state reduced single-electron density matrix and use it to calculate its absorption spectrum of polyacetylene oligomers.

Although the method can be applied to ab initio methods and various models, we here employ the Pariser–Parr–Pople (PPP) Hamiltonian to describe the electron in the polyacetylene oligomers. In the absence of the external fields, the π-electrons in the polyacetylene are well described by the PPP Hamiltonian [27–29],

$$H = H_{\text{SSH}} + H_{\text{C}} . \tag{3}$$

H_{SSH} is the Su–Schrieffer–Heeger (SSH) Hamiltonian, which consists of the Hückel Hamiltonian plus the electron–phonon coupling. H_{C} represents the Coulomb interaction among the π electrons and nuclei. We employ the same parameters in Ref. [2]. The geometry is fixed in the calculation. Here π-orbitals of N carbon atoms are employed as the basis set, and m and n represent π-orbitals at the sites m and n, respectively.

Assuming that a density matrix ρ is close to the HF ground-state reduced single-electron density matrix $\rho^{(0)}$, we may partition ρ into two parts:

$$\rho = \rho^{(0)} + \delta\rho , \tag{4}$$

Similarly, the approximate Fock matrix h may be decomposed in the form,

$$h = h^{(0)} + \delta h , \tag{5}$$

where $h^{(0)}$ is the Fock matrix for the HF ground state,

$$h_{nm}^{(0)} = t_{nm} + 2\delta_{n,m} \sum_l v_{nl} \rho_{ll}^{(0)} - v_{nm} \rho_{nm}^{(0)} , \tag{6}$$

$$\delta h_{nm} = 2\delta_{n,m} \sum_l v_{nl} \delta\rho_{ll} - v_{nm} \delta\rho_{nm} . \tag{7}$$

Here $\delta_{n,m} = 1$ is the Kronecker delta and Coulomb interaction v_{nm} is given by the Ohno formula [30]. We have thus,

$$
\begin{aligned}
A(\rho) &\equiv [h, \rho] = [h^{(0)} + \delta h, \rho^{(0)} + \delta\rho] \\
&= [h^{(0)}, \rho^{(0)}] + [h^{(0)}, \delta\rho] \\
&\quad + [\delta h, \rho^{(0)}] + O(\delta\rho^2)
\end{aligned} \tag{8}
$$

$$
\begin{aligned}
&= [h^{(0)}, \delta\rho] + [\delta h, \rho^{(0)}] + O(\delta\rho^2) \\
&= \mathscr{L}\delta\rho + O(\delta\rho^2) .
\end{aligned} \tag{9}
$$

where $\mathscr{L}$ is the linearized Liouville operator:

$$
\begin{aligned}
\mathscr{L}_{ij,mn} &\equiv \delta_{j,n} h_{im}^{(0)} - \delta_{i,m} h_{jn}^{(0)} + 2\delta_{m,n}(v_{in} - v_{jn})\rho_{ij}^{(0)} \\
&\quad - \delta_{i,m} v_{in} \rho_{jn}^{(0)} + \delta_{j,n} v_{jm} \rho_{im}^{(0)} .
\end{aligned} \tag{10}
$$

Since the density matrix ρ is close to the HF ground-state density matrix $\rho^{(0)}$, we may use this ρ as an initial guess to the ground-state density matrix. $\delta\rho$ may be evaluated via Eq. (9). And we thus have

$$\delta\rho \simeq (\mathscr{L} + i\bar{\Gamma})^{-1} A(\rho) , \tag{11}$$

where the damping term $i\bar{\Gamma}$ is introduced to ensure the convergence of ρ toward $\rho^{(0)}$, and $0 < \bar{\Gamma} \ll 1$. Denote that

$$\rho' = \rho - \text{Re}(\delta\rho) . \tag{12}$$

We use this ρ' as the new approximation to the $\rho^{(0)}$. Eq. (8) and Eq. (10) ∼ Eq. (12) may be iteratively used until any matrix element $|\delta\rho_{mn}|$ is less than a criteria $\delta\rho_c$, i.e., $|\delta\rho_{mn}| \leqslant \delta\rho_c$. The convergence is thus achieved and the current ρ' may be taken as an approximation to $\rho^{(0)}$.

Since $\rho^{(0)}$ satisfies the idempotency condition

$$\rho^{(0)} = \rho^{(0)} \rho^{(0)} , \tag{13}$$

we may impose the condition (13) on ρ' via the following equations [9,31]:

$$\rho'' = 3(\rho')^2 - 2(\rho')^3 \tag{14}$$

and ρ'' is thus the improved approximation to $\rho^{(0)}$. Eq. (14) may be used repeatedly until a convergence is reached, and $\rho^{(0)}$ is thus determined. The above procedure may be modified so that the computational time for $\rho^{(0)}$ scales linearly with the system size. As we have done in Refs. [1,2], we introduce: $\delta\rho_{i,j} = 0$ for $|i - j| > \alpha$ or $r_{ij} > l_1$ where r_{ij} is the distance between atom i and j. Here l_1 is chosen because $\delta\rho$ corresponds to the excited states. The same critical length l_1 can be applied to $h^{(0)}$ and δh. This leads to a reduction of the dimension of $\delta\rho$ or $\mathscr{L}$. For instance, in an one-dimensional system, the dimension is reduced from N^2 to $D_L \equiv (2\alpha + 1)N - \alpha(\alpha + 1)$, where α is the number of the atomic orbitals within the distance l_1. We denote the resulting reduced density matrix as $\delta\tilde{\rho}$, and arrange its elements

in the following increasing order: $\delta\tilde{\rho}_{1,1}$, $\delta\tilde{\rho}_{1,2}$, ..., $\delta\tilde{\rho}_{1,\alpha+1}$, $\delta\tilde{\rho}_{2,1}$, $\delta\tilde{\rho}_{2,2}$, ..., $\delta\tilde{\rho}_{2,\alpha+2}$, $\delta\tilde{\rho}_{3,1}$, ..., $\delta\tilde{\rho}_{N,N}$.

The third term on the r.h.s. of Eq. (10) contributes to $A(\rho)$ in Eq. (9) by

$$\sum_n 2(v_{in} - v_{jn})\rho_{ij}^{(0)}\delta\rho_{nn}. \tag{15}$$

Because of the cancellations between v_{in} and v_{jn} (caused by the 'nearsightedness' of $\rho^{(0)}$ [23,32]), and among different $\delta\rho_{nn}$, it is observed that the summation over n in Eq. (15) may be limited approximately between k_0 and k_1, where $k_0 = \max(1,\min(i - \alpha_c, j - \alpha_c))$, $k_1 = \min(\max(i + \alpha_c, j + \alpha_c), N)$. Here α_c is the number of the atomic orbitals within the distance l_c. The critical length l_c is for the summation in Eq. (15) and $l_c \sim l_1$ for our system. Therefore, lastly we keep only those third terms on the r.h.s. of Eq. (10) whose m or n runs between k_0 and k_1.

The combination of those approximations result in zero values of most $\mathcal{L}_{ij,mn}$. With the particular ordering of $\delta\tilde{\rho}$, the resulting Liouville matrix, denoted as $\tilde{\mathcal{L}}$, has a band diagonal form in one dimensional system [2]. There are $(2\beta + 1)D_L - \beta(\beta + 1)$ elements within the diagonal band of $\tilde{\mathcal{L}}$, where $\beta = 2\alpha\alpha_c + \alpha_c$. Eq. (9) thus becomes,

$$(\tilde{\mathcal{L}} + \mathrm{i}\bar{\Gamma})\delta\tilde{\rho} = \tilde{A}, \tag{16}$$

where $\tilde{A} = [h(\tilde{\rho}), \tilde{\rho}]$ and $\tilde{A}_{ij} = 0$ for $|i - j| > \alpha$. The band diagonal form of $\tilde{\mathcal{L}}$ enables us to solve

Table 1
Comparison between the LDM and exact HF ground-state energies

N	Energy HF (eV)	Energy LDM (eV)
40	− 243.7554	− 243.7531
60	− 366.0529	− 366.0490
80	− 488.3505	− 488.3450
100	− 610.6480	− 610.6410
140	− 855.2431	− 855.2330
200	− 1222.1358	− 1222.1211
300	− 1833.6235	− 1833.6012
400	− 2445.1113	− 2445.0813
500	− 3056.5990	− 3056.5615

Eq. (16) in the frequency domain via a simple $O(N)$ scaling algorithm [2]. Eq. (14) is then used iteratively to ensure the idempotency. The additional computational time is of $O(N)$ scaling as well.

It is very important to start with a good initial guess ρ to the ground-state reduced density matrix $\rho^{(0)}$. The following procedure, which is similar to that of Refs. [5,18], has been employed to determine ρ.

1. We determine the values of ρ_{ij} and ρ_{ji} where i is fixed and j includes all the nearby atomic orbitals that satisfies $r_{ij} \leqslant l_1$. This is achieved by performing a HF calculation for all the atoms within the range $r_{ij} \leqslant l_1$.
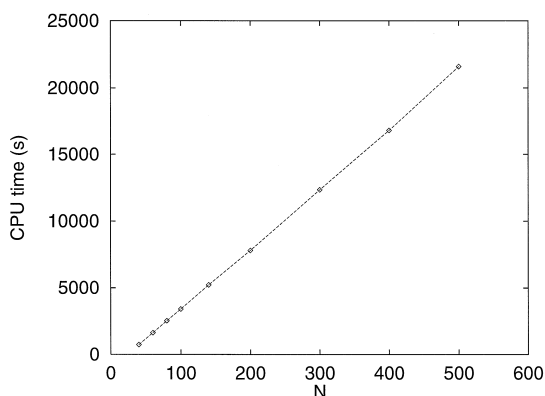2. The entire matrix ρ may be obtained by repeating the above (1) for all i.

Fig. 1. CPU time on an SGI Origin 200 workstation for 40, 60, 80, 100, 140, 200, 300, 400, and 500. $\Gamma = 0.001$ meV and $\alpha = 20$.
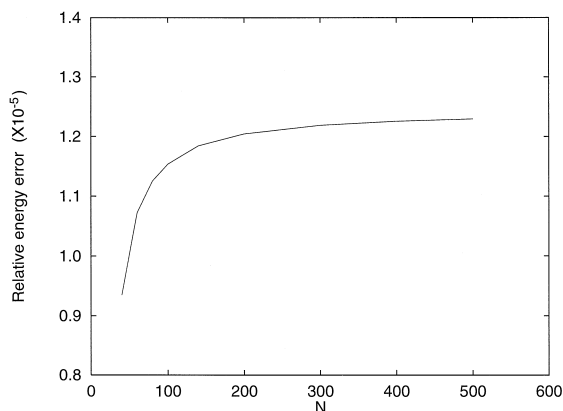

Fig. 2. Relative energy error r for 40, 60, 80, 100, 140, 200, 300, 400, and 500. $\bar{\Gamma} = 0.001$ meV and $\alpha = 20$.
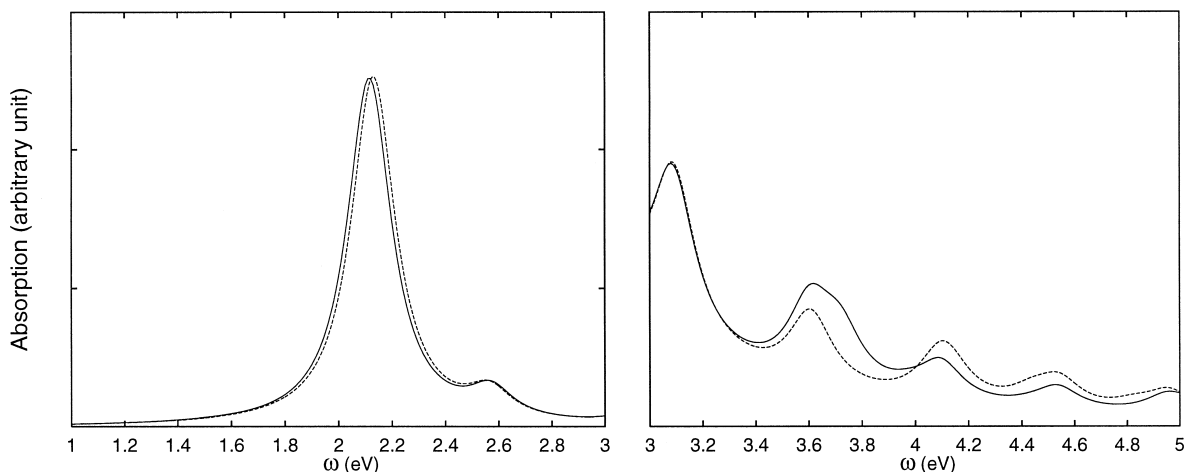
Fig. 3. Absorption spectra for $N = 60$. $\alpha = 20$. Solid line: the LDM method. The dashed line: the full TDHF calculation. The phenomenological dephasing constant $\Gamma = 0.1$ eV for excited states. The second figure is scaled $300/15$ times the first one.

The above procedure is applicable to any atomic systems, and is of $O(N)$ scaling. Since polyacetylene is quite uniform, the computational effort is reduced by performing the HF calculation once.

Fig. 1 shows that the computational time of the ground state goes linearly with increasing the size of the polymer. $\overline{\Gamma} = 0.001$ meV, $\alpha_0 = 20$, and $\delta\rho_c = 10^{-5}$ have been set in the calculation. Convergence is achieved after three iterations for $N = 40$ to 500. Idempotency condition is satisfied via applying (14) once with the criteria $|\rho''_{ij} - \rho'_{ij}| < 10^{-4}$ for all i and j.

To test the accuracy of our calculation, the comparison between the LDM and exact HF ground-state energies is given in Table 1. The ground-state energy calculated by LDM is in an excellent agreement with the exact HF ground-state energy for any oligomer with N between 40 and 500. The relative energy error versus the size is examined in Fig. 2. The relative energy error r is expressed as

$$r = \frac{E_{\text{HF}} - E_{\text{LDM}}}{E_{\text{HF}}} . \tag{17}$$

The value of r increases for $40 \leqslant N \leqslant 200$, and saturates for $N > 200$. This reflects the two facts: (i) the percentage of the cutoff reduced density matrix elements increases with N and the rate of increase is proportional inversely to N; and (ii) $\rho_{ij}^{(0)}$ goes to zero exponentially with increasing r_{ij}, i.e. the 'nearsightedness' of $\rho^{(0)}$ [23,32]. In this method,

computational accuracy is controlled by l_1, $\overline{\Gamma}$, and $\delta\rho_c$. Higher accuracy is attainable by larger l_1 and smaller $\overline{\Gamma}$ and $\delta\rho_c$.

The calculated absorption spectrum via the LDM is shown by the solid line in Fig. 3. The dashed line is for full TDHF. The computational times for the ground and excited state within the full TDHF calculation scale as $O(N^3)$ and $O(N^6)$, respectively. There is an excellent agreement between the two methods up to 3.5 eV in frequency. Better agreement for higher frequency may be obtained by increasing l_1.

Vanderbilt and co-workers have developed a linear-scaling method for ground state [9], in which the energy $E \equiv \text{tr}[\rho(h - \mu)]$ is minimized. In comparison, $[\rho,h]$ is set to zero via an numerical iterative procedure in the new frequency domain LDM method. The LDM method is only of $O(N)$ scaling for one-dimensional systems. For two- or three-dimensional systems, Eq. (9) may be solved in the time domain, and it is readily shown that the computational time should scale linearly with the system size [1,33]. Cut-off is employed in evaluation of Eq. (15), and this may be replaced by the fast multipole method (FMM) [22,34,35].

Acknowledgements

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