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Linear-scaling computation of ground state with time-domain localized-density-matrix method

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Abstract

Recently developed time-domain localized-density-matrix (LDM) method for calculating the electronic excited-state properties has been applied to calculate the electronic ground state. The computational time remains to scale linearly with the system size. To test the method, we use it to determine the ground states of polyacetylene oligomers containing up to 20000 carbon atoms. The Pariser–Parr–Pople (PPP) Hamiltonian is employed for the π electrons of the systems. Comparison to the conventional diagonalization shows the high efficiency as well as accuracy of the time-domain LDM method. © 1999 Elsevier Science B.V. All rights reserved.

Ab initio molecular orbital calculations are usually limited to small- and medium-size molecular systems. The obstacle lies in the rapid increasing of computational cost as the systems become larger and more complex. The computational time is proportional to a certain power of the system size, i.e., $t_{\mathrm{cpu}} \propto N^x$, where t_{cpu} is the computational time, N is the number of electronic orbitals, and x is some number which is usually larger than 1. For instance, the computational time of ab initio Hartree–Fock molecular orbital calculation has an $O(N^3)$ scaling. This obstacle has been removed in principle. Several linear scaling methods have been developed to calculate electronic ground states [1–21].

Recently a LDM method has been developed to calculate the excited-state properties of very large electronic systems with explicit inclusion of the electron–electron Coulomb interaction [22,23], 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. This method has also been applied to the PPP-like model based on non-orthonormal basis set [24]. Based on a similar idea, linear-scaling computation for the ground states of one-dimensional systems has been achieved in the frequency domain [25]. However, this frequency-domain linear-scaling LDM calculation is confined to the one-dimensional systems while general physical, chemical, and biological systems are three dimensional. Time-domain LDM method does not have such a restriction, and is applicable to two- and three-dimensional systems.

In this work, the time-domain LDM method is modified to determine the ground states of polyacetylene oligomers. The PPP Hamiltonian is employed to describe the π electrons in the systems. The linear-scaling behavior of the computational time

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is investigated. Comparison to the conventional Hartree–Fock diagonalization (HFD), which employs the same PPP Hamiltonian, is examined.

When an external electromagnetic field $\mathscr{E}(t)$ is applied to a polyacetylene oligomer, its π electrons response to the field, and optical signals may be observed. The π electrons in the polyacetylene are well described by the PPP Hamiltonian [26–28],

$$H = H_{\mathrm{SSH}} + H_{\mathrm{C}} + H_{\mathrm{ext}} . \tag{1}$$

H_{SSH} is the Su–Schrieffer–Heeger (SSH) Hamiltonian, which consists of the Hückel Hamiltonian plus electron–phonon coupling. H_{C} represents the Coulomb interaction among the π electrons and nuclei. H_{ext} is the interaction between the π electrons and an external electric field $\mathscr{E}(t)$. We employ the same parameters as those in Ref. [23]. The geometry is fixed in the calculation. N carbon π-orbitals are employed as the basis set, and m and n represent π-orbitals at the sites m and n, respectively. Within the TDHF approximation [29], a closed non-linear self-consistent equation of motion is yielded for the reduced single-electron density matrix $\rho(t)$,

$$\mathrm{i}\hbar \dot{\rho}(t) = \left[h(t) + f(t), \rho(t) \right] . \tag{2}$$

Here $h(t)$ is the Fock matrix:

$$h_{nm}(t) = t_{nm} + 2\delta_{n,m} \sum_{l} v_{nl}\, \rho_{ll}(t) - v_{nm}\, \rho_{nm}(t) , \tag{3}$$

where t_{nm} is the hopping matrix element between m and n, and v_{nm} is the Coulomb repulsion between two electrons at m and n, respectively. $f(t)$ describes the interaction between an electron and the external field $\mathscr{E}(t)$ [26].

The PPP–Hartree–Fock (PPP–HF) ground-state density matrix $\rho^{(0)}$ may be determined by the following equation [25],

$$\left[h^{(0)}, \rho^{(0)} \right] = 0 , \tag{4}$$

together with the idempotency requirement,

$$\rho^{(0)} \rho^{(0)} = \rho^{(0)} , \tag{5}$$

where $h^{(0)}$ is the Fock matrix when $\mathscr{E}(t) = 0$.

The TDHF Eq. (2) is usually used to simulate the electronic response to the external field. In this work it is modified to determine the PPP–HF ground state by setting $\mathscr{E}(t) = 0$ or $f(t) = 0$. Starting from an initial guess of the density matrix $\rho(t = t_0)$ at time $t = t_0$, we follow its time evolution by integrating the following equation

$$\mathrm{i}\left[\hbar \frac{\mathrm{d}}{\mathrm{d}t} + \gamma(t) \right] \rho(t) = \left[h(t), \rho(t) \right] . \tag{6}$$

$\gamma(t)$ is a phenomenological dephasing parameter. It is time dependent and approaches zero over the time. It is introduced to improve the calculation efficiency and ensure the eventual convergence $\rho(t)$ to $\rho^{(0)}$. $\gamma(t)$ may be of different forms, and we chose the following expression in our calculation,

$$\gamma(t) = \gamma_0 \frac{1}{1 + (t - t_0)/\bar{t}} , \tag{7}$$

where t_0 is the initial time and γ_0 is the dephasing parameter at $t = t_0$. $\bar{t}$ is the time constant which is approximately the simulation time. Since $\rho^{(0)}$ is real, we retain only the real part of $\rho(t)$ as the current approximate density matrix after each integration step of Eq. (6) over a time interval Δt. This accelerates the elimination of the excited-state components in $\rho(t)$, which can be seen by expanding $\rho(t)$ in terms of the eigenvectors ρ_ν of the Liouville operator [26,30,31]:

$$\rho(t) \simeq c_0\, \rho^{(0)} + \sum_{\nu} c_\nu \exp\left[-\mathrm{i}\,\omega_\nu t - \int \mathrm{d}t\, \gamma(t) \right] \rho_\nu , \tag{8}$$

where ω_ν is the frequency for the eigenvector ρ_ν and we assume that the difference between $\rho(t)$ and $\rho^{(0)}$ is small. Retaining only Re[$\rho(t)$] as the approximate density matrix reduces thus the excited-state components in $\rho(t)$ by extra factor $\cos(\omega_\nu t)$. The idempotency is then imposed by the following equation [5,32]:

$$\rho' = 3(\rho)^2 - 2(\rho)^3 . \tag{9}$$

Eq. (9) is repeated several times till a convergence is reached. The resulting ρ' is taken as the new approximate density matrix. The above process, which includes the integration of Eq. (6) over Δt, retaining of Re[$\rho(t)$] and imposing idempotency, is employed iteratively until the density matrix $\rho(t)$ is converged. Note that the initial guess is preferably close enough

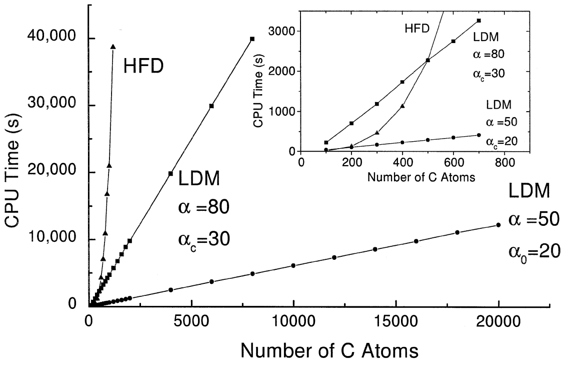

Fig. 1. Comparison between HFD and LDM CPU time on SGI Origin 200 workstation. (A) LDM: $\alpha = 80$ and $\alpha_c = 30$; and (B) LDM: $\alpha = 50$ and $\alpha_c = 20$.

to the real ground state density matrix $\rho^{(0)}$; otherwise a divergence may occur.

To achieve the linear-scaling computation of ground state, we adopt similar approximations as the linear-scaling LDM calculation for the excited states [22,23]. First, we set $\rho_{i,j}(t)$ to 0 for $|i-j| > \alpha$ or $r_{ij} > l_1$ (where r_{ij} is the distance between atoms i and j and l_1 is the critical length for the first induced density matrix [22,23]). The critical length l_1 is used instead of l_0 (which is the critical length of the ground-state reduced density matrix as defined in Ref. [22,23]) to ensure the convergence [25]. This is because that $\rho(t)$ contains contributions from the excited states. Secondly, we employ the same truncation as Refs. [22,25] to evaluate an electron–electron interaction contribution to the right-hand-side (rhs) of Eq. (6), namely $2\Sigma_k(v_{i,k} - v_{j,k})\rho_{i,j}\,\rho_{kk}$ is approximated by

$$2 \sum_{k_0 \leqslant k \leqslant k_1} (v_{i,k} - v_{j,k})\,\rho_{i,j}\,\rho_{kk}\,, \tag{10}$$

where k_0 and k_1 are given, respectively, by $k_0 = \max[1,\min(i - \alpha_c, j - \alpha_c)]$ and $k_1 = \min[1,\max(i + \alpha_c, j + \alpha_c)]$. α_c is the number of atomic orbitals within another critical length l_c which is less than l_1 for polyacetylene oligomers [22,24].

In our calculation, the convergence criteria for Eq. (6) is given by

$$\sum_{ij} \left| \sum_k \left(h_{ik}\,\rho_{kj} - \rho_{ik} h_{kj} \right) \right| /N < R_1\,, \tag{11}$$

and for Eq. (9)

$$\sum_{ij} | \rho'_{ij} - \rho_{ij} | /N < R_2\,. \tag{12}$$

$t_0 = -0.05$ fs, $\gamma_0 = 10^{-6}$ eV, $\bar{t} = 10$ fs, and $\Delta t = 0.138$ fs have been employed.

The CPU time comparison between HFD and LDM methods is given in Fig. 1. Two LDM calculations are examined: (A) $\alpha = 80$, $\alpha_c = 30$, $R_1 = 10^{-6}$ eV, and $R_2 = 10^{-9}$, (B) $\alpha = 50$, $\alpha_c = 20$, $R_1 = 10^{-3}$ eV and $R_2 = 10^{-9}$. For HFD we use the convergence criteria $R_1 = 10^{-6}$ eV. The simulation times for (A) and (B) are ~ 3 and ~ 0.5 fs, respectively. Linear-scaling of CPU time is demonstrated for both (A) and (B). A drastic saving of CPU time is achieved for the LDM method compared to the HFD. When N is small, the HFD method requires less time because a relatively large overhead is required for the LDM method. The crossover in CPU time appears at $N = 500$ and less than 200 for (A) and (B), respectively (see the insert of Fig. 1).

To assess the accuracy of our LDM calculation, we compare the ground-state energies of LDM with that of the HFD method. The relative energy error is expressed as:

$$r = \frac{E_{\mathrm{HFD}} - E_{\mathrm{LDM}}}{E_{\mathrm{HFD}}}\,, \tag{13}$$

and is shown in Fig. 2. $R_1 = 10^{-8}$ eV is employed here for HFD. This figure shows that the LDM ground-state energies is in an excellent agreement with those of the HFD for any oligomer with $N = 100 \sim 2000$. Note that the small energy difference

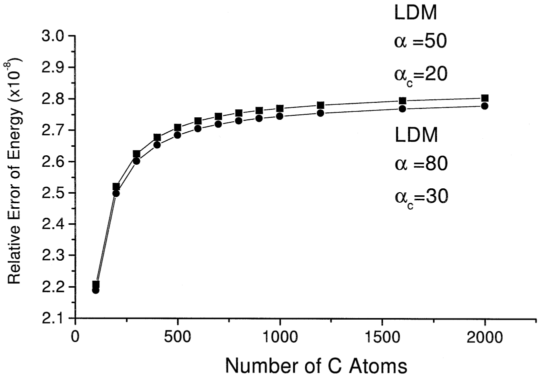

Fig. 2. Relative energy errors of two LDM calculations (A) and (B). Filled squares are for (A), and filled circles for (B).

between two sets of LDM parameters (A) and (B). We emphasize that (B) requires much less computational effort while the same high accuracy is achieved compared to (A).

The second approximation Eq. (10) has been shown to be an extremely good one for polyacetylene [24], and our current result provides the further evidence (see Fig. 2). The justification of the approximation comes mainly from the cancellation which is caused by the charge conservation [24]. The fast multiple method (FMM) has been used to calculate the summation of Coulomb interaction [17,33,34], and its computational timescales linearly with the system size [17,34]. It may be an alternative way to replace the second approximation [35]. As we have pointed out in Ref. [25], Eq. (4) have to be satisfied for calculating the excited-state properties within the TDHF approximation. The time-domain LDM method clearly satisfies this condition with the required accuracy. Resulted ground state density matrix and Fock matrix may be thus used for the excited-state TDHF calculation [35].

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