

## Linear scaling calculation of excited-state properties of polyacetylene

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A new method based on the equation of motion (EOM) for the reduced single-electron-density matrix is developed to calculate the excited-state properties of very large electronic systems. When the distance between two local orbitals is larger than a critical length, the corresponding off-diagonal density-matrix element is negligible and may be set to zero. This reduces the dimension of the EOM and the number of required matrix elements. The computational cost scales thus linearly with the system size. As an illustration, the new method is implemented to evaluate the absorption spectra of polyacetylene oligomers containing 30–500 carbon atoms. The resulting spectra agree well with those of the full calculation, and more importantly, the linear scaling of the computational time versus the size is clearly demonstrated. [S0163-1829(99)01611-2]

There is a growing interest in calculating the electronic structures of complex and large systems like protein and organic aggregates. *Ab initio* molecular-orbital and semiempirical calculations are usually limited to small or medium size molecular systems. The obstacle lies in the rapid increasing of computational costs as the systems become larger and more complex. The computational time  $t_{cpu}$  is proportional to a certain power of the system size, i.e.,  $t_{cpu} \propto N^x$ , where  $N$  is the number of electronic orbitals, and  $x$  is an exponent that is usually larger than 1. For instance, *ab initio* Hartree-Fock molecular-orbital calculation is a  $O(N^3)$  scaling method (i.e.,  $x=3$ ). To determine the electronic structures of very large systems, it is essential that the computational cost scales linearly with  $N$ . Several linear scaling methods have been developed to calculate ground electronic states.<sup>1–23</sup> The physical basis of these methods is “the nearsightedness of equilibrium systems.”<sup>24</sup> However, the excited states of very large electronic systems are much more difficult to calculate. Several linear scaling calculations based on noninteracting electron models have been carried out for excited states<sup>10,25</sup> and for the static electronic response.<sup>26,27</sup> To our knowledge, no linear scaling calculation that includes explicitly electron-electron Coulomb interaction has been implemented for the excited states.

A reduced single-electron density matrix  $\rho$  contains important information of an electronic system. The diagonal element  $\rho_{ii}$  is the electron density at a local orbital  $i$ , and the off-diagonal element  $\rho_{ij}$  ( $i \neq j$ ) measures the electronic coherence between two local orbitals  $i$  and  $j$ , where  $\rho_{ij} = \langle \hat{a}_j^\dagger \hat{a}_i \rangle$ , and  $\hat{a}_j^\dagger$  and  $\hat{a}_i$  are the creation and annihilation operators at  $j$  and  $i$ , respectively. An EOM for a reduced density matrix has been used to calculate linear and nonlinear electronic responses to external fields<sup>28</sup> and, thus, probe the properties of excited states. This EOM is based on the time-dependent Hartree-Fock (TDHF) approximation,<sup>29</sup> and the time for its solution scales as  $O(N^6)$ . The TDHF includes the complete single-electron excitations and some partial double, triple, and other multielectron excitations. It has been applied successfully to investigate the optical properties of conjugated polymers.<sup>28</sup> Recently a  $O(N^2)$  scaling density-matrix–spectral-moment algorithm<sup>30</sup> has been developed to calculate the envelope of the entire linear and nonlinear optical spectra of conjugated polymers containing up to 300 carbon atoms. In Ref. 31 it has been shown that off-

diagonal elements  $\rho_{ij}$  are negligible when the distance  $r_{ij}$  between  $i$  and  $j$  is larger than a critical length  $l_0$ . This is a consequence of “the nearsightedness of equilibrium systems.”<sup>24</sup> When the system is subjected to an external field  $\mathcal{E}(t)$ , the field induces a change  $\delta\rho$  in the reduced density matrix. The induced density matrix  $\delta\rho$  has a similar “nearsightedness,” i.e., off-diagonal element  $\delta\rho_{ij}$  is approximately zero as the distance between  $i$  and  $j$  is large enough.<sup>31</sup> Different orders of responses in  $\mathcal{E}(t)$  have different critical lengths. Usually the higher the order of response  $n$  is, the longer the critical length  $l_n$  is, i.e.,  $l_0 < l_1 < l_2 < l_3 < \dots$ . We may truncate the  $n$ th order induced density-matrix response  $\delta\rho^{(n)}$  [note,  $\delta\rho = \delta\rho^{(1)} + \delta\rho^{(2)} + \delta\rho^{(3)} + \dots$ ] by setting its elements  $\delta\rho_{ij}^{(n)}$  to zero for  $r_{ij} > l_n$ . This truncation may lead to a drastic reduction of the computational time.

In this paper, we concentrate on the first-order response and report a new method for calculating linear optical properties of very large electronic systems. The method is based on the truncation of reduced density matrix mentioned above, and its computational time scales linearly with the system size  $N$ . It is a general method and does not rely on specific approximation for the electron correlation. As its first application, we develop it within the TDHF approximation. To demonstrate its validity, we implement the method to determine the absorption spectra of polyacetylene oligomers containing up to 500 carbon atoms. Although a more accurate and general Hamiltonian may be used,<sup>32</sup> we employ a semiempirical Hamiltonian, the Parisa-Parr-Pople (PPP) Hamiltonian, to describe the  $\pi$  electrons of the system. In the rest of the paper the TDHF approximation is briefly introduced followed by the formalism of the new method. The results of our calculation on polyacetylene oligomers are presented and analyzed next. Finally, further development of the method is discussed and a summary is given.

When an external electromagnetic field is applied to a polyacetylene oligomer, its  $\pi$  electrons response to the field, and the optical signals may be observed. The  $\pi$  electrons may be characterized by the PPP Hamiltonian,<sup>28,33</sup>

$$H = H_{SSH} + H_C + H_{ext}. \quad (1)$$

$H_{SSH}$  is the Su-Schrieffer-Heeger (SSH) Hamiltonian, which consists of the Hückel Hamiltonian with electron-phonon

coupling.  $H_C$  represents the Coulomb interaction among  $\pi$  electrons or nuclei, which is described by the Ohno formula.<sup>34</sup>  $H_{\text{ext}}$  is the interaction between  $\pi$  electrons and the external electric field  $\mathcal{E}(t)$ . We employ the same parameters as those in Ref. 28. The double and single bond lengths are 1.47 Å and 1.35 Å, respectively, and the bond angle is 120°. Because there is a symmetry between spin up and spin down in the system, we omit the spin index. The reduced single-electron density-matrix element  $\rho_{ij}(t)$  obeys the Heisenberg equation of motion, where  $i$  ( $j$ ) represents  $\pi$  orbital at carbon atom  $i$  ( $j$ ). We label the carbon atoms in an increasing numerical order from one end of an oligomer to the other. With the TDHF approximation, a closed nonlinear self-consistent EOM is yielded for the reduced single-electron density matrix  $\rho(t)$

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

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

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

with  $t_{nm}$  being the hopping matrix element between  $m$  and  $n$ , and  $v_{nm}$  the Coulomb repulsion between two electrons at  $m$  and  $n$ , respectively.  $f(t)$  represents the interaction between an electron and the external field  $\mathcal{E}(t)$ ,

$$f_{nm}(t)=\delta_{n,m}ez(n)\mathcal{E}(t). \quad (4)$$

We partition the density matrix  $\rho(t)$  into two parts:

$$\left( \begin{array}{cccccccc} \delta\rho_{1,1}^{(1)} & \delta\rho_{1,2}^{(1)} & \cdots & \delta\rho_{1,\alpha_1+1}^{(1)} & 0 & 0 & \cdots & 0 \\ \delta\rho_{2,1}^{(1)} & & & & \delta\rho_{2,\alpha_1+2}^{(1)} & 0 & \cdots & 0 \\ \vdots & & \ddots & & & \ddots & \ddots & \vdots \\ \delta\rho_{\alpha_1+1,1}^{(1)} & & & & & & & \vdots \\ 0 & \delta\rho_{\alpha_1+2,2}^{(1)} & & & & & & \\ 0 & 0 & \ddots & & & & \ddots & \\ & & \ddots & & & & \ddots & 0 \\ \vdots & \vdots & & & & & & \delta\rho_{N-\alpha_1,N}^{(1)} \\ & & & & \ddots & \ddots & & \vdots \\ 0 & 0 & \cdots & & 0 & \delta\rho_{N,N-\alpha_1}^{(1)} & \cdots & \delta\rho_{N,N}^{(1)} \end{array} \right), \quad (10)$$

where  $\alpha_1$  is the number of bonds within the critical length  $l_1$ . Only those elements  $\delta\rho_{ij}^{(1)}$  within the diagonal band of  $\delta\rho^{(1)}$  need to be considered explicitly. This leads to a reduction of the dimension of  $\delta\rho^{(1)}$  or  $\mathcal{L}$  from  $N^2$  to  $D_L \equiv (2\alpha_1 + 1)N - \alpha_1(\alpha_1 + 1)$ . We denote the resulting reduced first-order density matrix as  $\delta\tilde{\rho}^{(1)}$  and arrange its elements in the following increasing order:  $\delta\rho_{1,1}^{(1)}, \delta\rho_{1,2}^{(1)}, \dots, \delta\rho_{1,\alpha_1+1}^{(1)}, \delta\rho_{2,1}^{(1)}, \delta\rho_{2,2}^{(1)}, \dots, \delta\rho_{2,\alpha_1+2}^{(1)}, \delta\rho_{3,1}^{(1)}, \dots, \delta\rho_{N,N}^{(1)}$ .

Secondly,  $\rho_{ij}^{(0)}$  is set to zero for  $r_{ij} > l_0$ . [We denote the

$$\rho(t)=\rho^{(0)}+\delta\rho(t), \quad (5)$$

where  $\rho^{(0)}$  is the single-electron density matrix representing the Hartree-Fock ground state in the absence of the external field, and  $\delta\rho(t)$  is the difference between  $\rho(t)$  and  $\rho^{(0)}$ , i.e., the induced density matrix by the external field  $\mathcal{E}(t)$ . Similarly, the Fock matrix  $h(t)$  is decomposed in the form

$$h(t)=h^{(0)}+\delta h(t), \quad (6)$$

where  $h^{(0)}$  is the Fock matrix when  $\mathcal{E}(t)=0$ . Equation (2) thus becomes

$$i\hbar\dot{\delta\rho}-\mathcal{L}\delta\rho=[f,\rho^{(0)}]+[f,\delta\rho]+[\delta h,\delta\rho], \quad (7)$$

where  $\mathcal{L}$  is the so-called Liouville matrix and is defined as

$$\begin{aligned} \mathcal{L}_{ij,mn} \equiv & \delta_{j,n}h_{im}^{(0)} - \delta_{i,m}h_{jn}^{(0)} + 2\delta_{m,n}(v_{in} - v_{jn})\rho_{ij}^{(0)} \\ & - \delta_{i,m}v_{in}\rho_{jn}^{(0)} + \delta_{j,n}v_{jm}\rho_{im}^{(0)}. \end{aligned} \quad (8)$$

For the first-order induced density matrix  $\delta\rho^{(1)}$ , its dynamics may be described by the following equation,

$$i\hbar\dot{\delta\rho}^{(1)}-\mathcal{L}\delta\rho^{(1)}=[f,\rho^{(0)}]. \quad (9)$$

The key for the  $O(N)$  scaling lies in the reduction of the sizes of  $\delta\rho^{(1)}$  and  $\mathcal{L}$ . This reduction is due to three approximations. First,  $\delta\rho_{ij}^{(1)}$  is approximately zero when  $r_{ij} > l_1$ . This approximation leads to a band diagonal form of  $\delta\rho^{(1)}$ , which may be expressed as follows,

resulting ground-state density matrix as  $\tilde{\rho}^{(0)}$ .] Consequently  $h_{ij}^{(0)}$  becomes zero for the same  $r_{ij}$  [see Eq. (3)]. Moreover, this leads to vanishing values of most first, second, fourth, and fifth terms on the right-hand side (rhs) of Eq. (8).

The third term on the rhs of Eq. (8) contributes to  $\delta\dot{\rho}_{ij}^{(1)}$  in Eq. (9) by

$$\sum_n 2(v_{in} - v_{jn})\rho_{ij}^{(0)}\delta\rho_{nn}^{(1)}. \quad (11)$$

Because of the cancellations between  $v_{in}$  and  $v_{jn}$  [caused by the ‘‘nearsightedness’’ of  $\rho^{(0)}$ ], and among different  $\delta\rho_{nn}^{(1)}$ , it is observed that the summation over  $n$  in Eq. (11) 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  $\alpha_c$  is a cutoff length for the summation in Eq. (11) and  $\alpha_c \sim \alpha_1$  for our system. Therefore, lastly, we

keep only those third terms on the rhs of Eq. (8) whose  $m$  or  $n$  is between  $k_0$  and  $k_1$ .

The combination of the second and third approximations results in zero values of most  $\mathcal{L}_{ij,mn}$ . With the particular ordering of  $\delta\tilde{\rho}^{(1)}$ , the resulting Liouville matrix, denoted as  $\tilde{\mathcal{L}}$ , has a band diagonal form as follows,

$$\begin{pmatrix} L_{1,1} & L_{1,2} & \cdots & L_{1,\beta+1} & 0 & 0 & \cdots & 0 \\ L_{2,1} & & & & L_{2,\beta+2} & 0 & \cdots & 0 \\ \vdots & & & & & \ddots & & \vdots \\ L_{\beta+1,1} & & & & & & & \vdots \\ 0 & L_{\beta+2,2} & & & & & & \vdots \\ 0 & 0 & \ddots & & & & & 0 \\ \vdots & \vdots & & & & & & \vdots \\ 0 & 0 & \cdots & & & & & L_{D_L-\beta, D_L} \\ & & & & & & & \vdots \\ & & & & & & & L_{D_L, D_L} \end{pmatrix}. \quad (12)$$

There are  $(2\beta+1)D_L - \beta(\beta+1)$  elements within the diagonal band of  $\tilde{\mathcal{L}}$ , where  $\beta = 2\alpha_1\alpha_c + \alpha_c$ . Equation (9) thus becomes

$$i\hbar \delta\tilde{\rho} - \tilde{\mathcal{L}}\delta\tilde{\rho}^{(1)} = [f, \tilde{\rho}^{(0)}]. \quad (13)$$

Although it is not essential for the  $O(N)$  scaling, the band diagonal form of  $\tilde{\mathcal{L}}$  enables us to solve Eq. (13) in the frequency domain via a simple  $O(N)$  scaling algorithm. We adopt a Gaussian elimination procedure with back substitution. The procedure consists of two processes: the forward process, which eliminates the lower half of  $\tilde{\mathcal{L}}$ , and the backward process, which evaluates each variable. Detailed analysis shows that the total number of algebraic operations is approximately

$$2(\beta+1)^2 D_L. \quad (14)$$

In the calculation,  $\alpha_1$  and  $\alpha_c$  are fixed. Since  $D_L \sim O(N)$ , the total computational time scales thus linearly with  $N$ . Further analysis demonstrates that the total memory needed for  $\tilde{\mathcal{L}}$  is  $(2\beta+1)D_L - \beta(\beta+1)$  and also scales as  $O(N)$ .

The accuracy of calculation is determined by the values of  $\alpha_1$ ,  $\alpha_0$ , and  $\alpha_c$ . For simplicity, we chose  $\alpha_0 = \alpha_c = \alpha_1 = \alpha$  in our calculation. We calculate the absorption spectrum for  $N = 40$  using  $\alpha = 20$ . The result is plotted in Fig. 1. The solid line is the resulting spectrum. To examine the accuracy of the calculation, we perform a full TDHF calculation for the same oligomer (i.e.,  $\alpha = 39$ ). The diamonds represent the results of the full TDHF calculation. The energy and intensity differences of the first peak between  $\alpha = 20$  and the full TDHF are 0.33 and 0.08 %, respectively. These calculations show that  $\alpha_0 = \alpha_c = \alpha_1 = 20$  gives accurate results. The reduced density matrix corresponding to a particular excitation has its ‘‘nearsightedness’’ and critical length. The critical length does not alter with increasing  $N$ , when  $N$  is much larger than the critical length. Thus the same value of  $\alpha_0$ ,  $\alpha_1$ , and  $\alpha_c$  may be used for different  $N$ , provided that

$N$  is large enough. The roles of different critical lengths have been investigated, and the details will be presented in another paper.<sup>35</sup> In the rest of the calculation, the same value of  $\alpha_1$ ,  $\alpha_0$ , and  $\alpha_c$  are adopted. The absorption spectrum for  $N = 500$  is determined. Its first peak redshifts and appears at  $\omega = 2.03$  eV. This is consistent with previous calculations.<sup>28</sup>

In Fig. 2 we examine the  $O(N)$  scaling of computational time and plot the CPU time versus  $N$ . The computational time spent in solving the Hartree-Fock ground state is negligible. The total CPU time is approximately the time needed for obtaining the excited-state properties. Clearly, the CPU time scales linearly with  $N$  for  $N$  between 30 and 500. The linear scaling of computational time for the excited-state properties has been convincingly achieved.

In the third approximation, the cancellation among different  $\delta\rho_{nn}^{(1)}$  is based on charge conservation, i.e.,  $\sum_n \delta\rho_{nn}^{(1)} = 0$ .

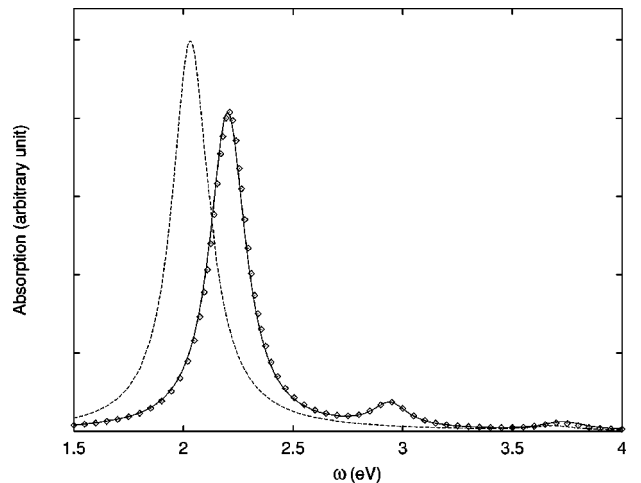


FIG. 1. Absorption spectra for  $N=40$  and 500. The solid line is for  $N=40$  and  $\alpha=20$ , and the dashed line for  $N=500$  and  $\alpha=20$ . The results of the full TDHF calculation for  $N=40$  are given by diamonds. The phenomenological dephasing constant  $\Gamma = 0.1$  eV. For comparison, all data for  $N=40$  are multiplied by 12.5.

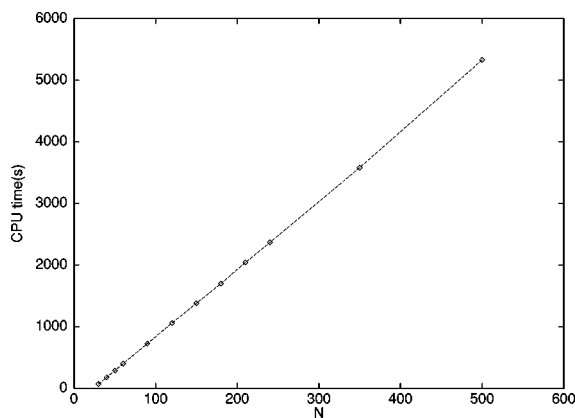


FIG. 2. CPU time on an SGI Indigo2 R10000 workstation for  $N=30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 350,$  and  $500$ . Each calculation is performed at a frequency  $\omega=2.175$  eV with  $\Gamma=0.1$  eV.  $\alpha=20$  is used.

The introduction of the cutoff  $\alpha_c$  and its value is further justified by the accuracy of our calculation (see Fig. 1). When the cancellation is strong,  $\alpha_c \approx \alpha_0$ ; when the cancellation is weak,  $\alpha_c \gg \alpha_0$  is expected. The fast multiple method (FMM) has been used to calculate the summation of Coulomb interaction,<sup>20,36,37</sup> and its computational time scales linearly with the system size  $N$ .<sup>20,37</sup> It may be an alternative to calculate Eq. (11). Although the band diagonal form is utilized to achieve the  $O(N)$  scaling, it is not essential. The key to the linear scaling is the reduction of the sizes of  $\delta\rho$  and  $\mathcal{L}$ . When Eq. (13) is solved in the time domain, it may be readily demonstrated that the solution is of the  $O(N)$  scaling, and the band diagonal form of  $\tilde{\mathcal{L}}$  is not required.<sup>35</sup> Therefore, the method may be extended to two- and three-dimensional systems, and a variety of physical, chemical, or biological systems may be investigated. To probe more excited states, we may generalize our current method for higher-order responses. For first-order response, only the first term on the

rhs of Eq. (7) contributes. For higher-order responses, the second and third terms on the rhs contribute as well. With the truncation of density matrix and Fock matrix, the computational time spent in evaluating the second and third terms is proportional to  $N$ . The computation for higher-order responses is of the  $O(N)$  scaling as well. In our calculation, the Hartree-Fock ground state is obtained first. This part of the calculation scales as  $O(N^3)$ . However, compared with the total time, its computational time is trivial for  $N=30-500$ . Combining our method for the excited states with existing algorithms for the ground state<sup>1-23</sup> would lead to a linear scaling of the total computational time, provided that the geometry is fixed during the calculation. We adopt a PPP Hamiltonian to describe the  $\pi$  electrons in polyacetylene and ignore differential overlaps of Coulomb interaction. Inclusion of the differential overlaps does not affect the  $O(N)$  scaling.<sup>32</sup> Therefore, we may generalize our method for implementation at *ab initio* calculation levels. An important point in our calculation is that no further approximation is made for the Hamiltonian. The only approximations made relate to the feature of reduced density matrix. This fact guarantees the wide applicability of the new method.

To summarize, we present a first linear scaling calculation that includes explicitly the Coulomb interaction for linear optical response of an electronic system. The linear scaling is achieved for the computational time as well as the memory required. This makes it possible for accurate numerical determination of the excited-state properties of very large electronic systems. Although the linear response has been the focus, nonlinear response may easily be evaluated via a slight generalization of the method.

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