

# An Efficient Implementation of the Direct Random-Phase Approximation Using the Quasi-Particle Formalism<sup>†</sup>

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An efficient direct integral-driven algorithm for the random-phase approximation (RPA) is introduced using the equation of motion on a transition density matrix representing a “quasi particle”. In the algorithm, several roots are obtained at the same time by solving a set of coupled equations that are projected on a space spanned by a set of error vectors representing the quasi particles. The most time-consuming RPA operation on the vectors is accomplished by a single call of an integral-generation routine, and the time per iteration is comparable to that for a direct SCF cycle. The algorithm is implemented using a new integral package based on accompanying coordinate expansion (ACE), as well as traditional integral routines from GAMESS. The example applications indicate good convergence of the iterative scheme. In some computationally intensive cases, the RPA computation for several excited states is completed in less time than the SCF computation.

## Introduction

The recent advent of powerful computational tools has significantly changed materials research. Particularly, quantum chemical computations of molecules and molecular aggregates provide very important information about the materials that might not be accessible otherwise. Many quantum chemical methods have been developed and implemented for efficient computation of the ground-state energy of large molecular systems typical in materials research. Advances in the development and implementation of algorithms for excited-state computations for such large molecular systems have been achieved to a lesser extent. The random-phase approximation (RPA) is certainly one of the most popular and important methods for computing the excited states of molecules.<sup>1–3</sup> It is popular because several excited states are obtained directly with relatively modest computational effort even for large molecular systems. The recent, rapid change in the computational environment has promoted efforts to develop and implement direct integral-driven algorithms. The direct integral-driven RPA has been developed and implemented by several groups.<sup>4–13</sup> In a direct algorithm, the RPA matrix is not explicitly evaluated, but the vectors resulting from the RPA operation are evaluated and stored. The RPA operation is accomplished by tracing trial vectors and integrals. In direct integral-driven schemes, entire integrals are evaluated for each iteration, instead of being computed once and stored in low-speed storage space. Therefore, the direct and direct integral-driven schemes require much less storage space. Of course, we need to pay for this advantage by repeating the computationally demanding integral evaluation for each iteration. We introduce an efficient direct RPA algorithm for obtaining several roots at a time. In the algorithm, one iteration requires almost the same computational effort as one Hartree–Fock (HF) self-consistent field (SCF) cycle. Because the iterative scheme for the RPA typically converges quite well, the computation time is almost equivalent to, or even smaller than, that of the SCF calculations.

## Theory and Computational Algorithm

The equation of motion (EOM) for the transition density matrix  $\bar{\rho}(r, r')$  in the frequency domain is

$$[H, \bar{\rho}(r, r')] = \bar{\rho}(r, r')\omega \quad (1)$$

The Hamiltonian can be decomposed as

$$H = f + V_N \quad (2)$$

where  $f$  is a one-body Fock operator composed of the zeroth-order Hartree–Fock (HF) density matrix and  $V_N$  is a two-body operator defined as the normal product with respect to the zeroth-order HF reference state. The transition density matrix  $\bar{\rho}(r, r')$  represents the transition of an electron between  $r$  and  $r'$  upon excitation and may be expressed as a superposition of HF particle–hole states. Equation 1 can also be seen as an EOM for the “quasi particle” (QP) represented by the transition density matrix. We construct the HF particle–hole and hole–particle states using binary products of the zeroth-order HF vacant and occupied orbitals  $\phi_a(r)\phi_i(r')$  and  $\phi_a(r')\phi_i(r)$ . Therefore,

$$[f, \bar{\rho}_k] = \Delta_k \quad (3)$$

where  $\bar{\rho}_k$  is the  $k$ th element of the zeroth-order transition density matrices in particle–hole and hole–particle space defined by the zeroth-order HF orbitals and  $\Delta_k = \epsilon_a - \epsilon_i$  with the orbital energies  $\epsilon_a$  and  $\epsilon_i$ . The  $f$  operator need not be diagonal but fulfills eq 3 for particle–hole and hole–particle transition density matrices. Projecting the equation onto particle–hole and hole–particle space, we have the familiar RPA equation for a set of transition densities oscillating with an eigenfrequency  $\omega_l$ .

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{Z}_l \\ \mathbf{Y}_l \end{bmatrix} = \pm \begin{bmatrix} \mathbf{Z}_l \\ \mathbf{Y}_l \end{bmatrix} \omega_l \quad (4)$$

Here, the elements of the Hamiltonian between pairs of particle–hole  $\{a, i\}$ ,  $\{b, j\}$  and hole–particle  $\{i, a\}$ ,  $\{j, b\}$  transition density matrices are

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$$A_{ai,bj} = \Delta_k + [\phi_a^*(r)\phi_i(r)|\phi_j^*(r')\phi_b(r')] - [\phi_a^*(r)\phi_b(r)|\phi_j^*(r')\phi_i(r')] \quad (5a)$$

$$B_{ai,bj} = [\phi_a^*(r)\phi_i(r)|\phi_b^*(r')\phi_j(r')] - [\phi_a^*(r)\phi_j(r)|\phi_b^*(r')\phi_i(r')] \quad (5b)$$

A set of the transition density matrices  $[\tilde{Z}_I^Z]$  corresponds to the  $I$ th eigenvector in eq 1 with an associating eigenvalue  $\omega_I$ . The RPA operations  $\mathbf{AZ}$ ,  $\mathbf{BZ}$ ,  $\mathbf{AY}$ , and  $\mathbf{BY}$  correspond to contractions of the Hamiltonian with the transition density matrices. We see that the  $V_N$  component is not diagonal and that the particle–hole transition density matrices (represented by  $\mathbf{Z}$ ) interact not only with themselves but also with the hole–particle transition density matrices (represented by  $\mathbf{Y}$ ) through this term. The problem can be also rewritten as a set of coupled equations.

$$(\mathbf{A} + \mathbf{B})(\mathbf{Z}_I + \mathbf{Y}_I) = (\mathbf{Z}_I - \mathbf{Y}_I)\omega_I \quad (6a)$$

$$(\mathbf{A} - \mathbf{B})(\mathbf{Z}_I - \mathbf{Y}_I) = (\mathbf{Z}_I + \mathbf{Y}_I)\omega_I \quad (6b)$$

with a bi-orthonormal condition

$$(\tilde{\mathbf{Z}}_I + \tilde{\mathbf{Y}}_I)(\mathbf{Z}_I - \mathbf{Y}_I) = \delta_{II} \quad (7)$$

Here, we see that the oscillation in particle–hole creation and annihilation is expressed as a coupling of symmetric (real)  $\mathbf{Z} + \mathbf{Y}$  and antisymmetric (imaginary)  $\mathbf{Z} - \mathbf{Y}$  modes. This expression is computationally more convenient because we can work on real symmetric and antisymmetric matrices instead of general nonsymmetric forms of matrices. Indeed, the RPA operations  $(\mathbf{A} + \mathbf{B})(\mathbf{Z} + \mathbf{Y})$  and  $(\mathbf{A} - \mathbf{B})(\mathbf{Z} - \mathbf{Y})$  can be accomplished using ordinary real Fock matrix formation algorithms with a minor modification for the antisymmetric mode. As the number of HF particle–hole states increases, the dimensions of  $\mathbf{A} + \mathbf{B}$  and  $\mathbf{A} - \mathbf{B}$  also increase. Straightforward diagonalization of eq 4 in the particle–hole and hole–particle spaces or the corresponding solution of eq 6 becomes more demanding.

We interpret the transition associated with an excitation energy  $\omega_I$  in terms of quasi particles that interact with each other. A QP is iteratively defined as an elemental excitation with which a particular transition is described. In other words, a set of QPs, whose dimension is much smaller than the total HF particle–hole space, fulfils eq 4 or eq 6 for a particular excitation. We solve the corresponding equations by a series of transformations within a subspace spanned by a set of bi-orthonormal vectors  $\mathbf{b}$  and  $\mathbf{c}$  representing the QPs.

$$\mathbf{G}^S \mathbf{U} = \mathbf{U} \mathbf{X} \quad (8a)$$

$$\mathbf{W}^2 = \mathbf{X}^{1/2} \tilde{\mathbf{U}} \mathbf{G}^A \mathbf{U} \mathbf{X}^{1/2} \quad (8b)$$

$$\mathbf{W}^2 \mathbf{V} = \mathbf{V} \omega^2 \quad (8c)$$

$$\mathbf{S} = \mathbf{U} \mathbf{X}^{-1/2} \mathbf{V} \omega^{1/2} \quad (8d)$$

$$\mathbf{T} = \mathbf{U} \mathbf{X}^{1/2} \mathbf{V} \omega^{-1/2} = (\tilde{\mathbf{S}})^{-1} \quad (8e)$$

Here,

$$\mathbf{G}^S = \tilde{\mathbf{b}}(\mathbf{A} + \mathbf{B})\mathbf{b} \quad (9a)$$

$$\mathbf{G}^A = \tilde{\mathbf{c}}(\mathbf{A} - \mathbf{B})\mathbf{c} \quad (9b)$$

$$\mathbf{S} = \tilde{\mathbf{c}}(\mathbf{Z} + \mathbf{Y}) \quad (10a)$$

$$\mathbf{T} = \tilde{\mathbf{b}}(\mathbf{Z} - \mathbf{Y}) \quad (10b)$$

and  $\sim$  indicates the transpose of a matrix.

Therefore, the problem of seeking a bi-orthonormal set of vectors  $\mathbf{Z} + \mathbf{Y}$  and  $\mathbf{Z} - \mathbf{Y}$  is converted to a problem of seeking a bi-orthonormal set of vectors  $\mathbf{b}$  and  $\mathbf{c}$ . The  $\mathbf{b}$  and  $\mathbf{c}$  vectors are chosen in an iterative fashion for a manifold spanned by  $\mathbf{b} = \mathbf{b} + \delta\mathbf{b}$  and  $\mathbf{c} = \mathbf{c} + \delta\mathbf{c}$  to fulfill eq 6 with  $\delta\mathbf{b}$  and  $\delta\mathbf{c}$  as small as possible.

$$(\mathbf{A} + \mathbf{B})\mathbf{bS}_I - \mathbf{cT}_I\omega_I = \delta\mathbf{cT}\omega_I - (\mathbf{A} + \mathbf{B})\delta\mathbf{bS} \approx \omega_I\delta\mathbf{c} - \Delta^S\delta\mathbf{b} = 0 \quad (11a)$$

$$(\mathbf{A} - \mathbf{B})\mathbf{cT}_I - \mathbf{bS}_I\omega_I = \delta\mathbf{bS}\omega_I - (\mathbf{A} - \mathbf{B})\delta\mathbf{cT} \approx \omega_I\delta\mathbf{b} - \Delta^A\delta\mathbf{c} = 0 \quad (11b)$$

Here,  $\Delta^S$  and  $\Delta^A$  are matrices consisting of the diagonal elements of the respective Hamiltonians. There are several choices in partitioning the Hamiltonian in eq 11 in order to solve for  $\delta\mathbf{b}$  and  $\delta\mathbf{c}$ . One choice is to take the full diagonal element of the Hamiltonians. Another choice is to take only the zeroth-order part  $\Delta$  to approximate the Hamiltonians, and we employ the latter choice here.

$$\delta\mathbf{b}_I = \frac{\omega_I[(\mathbf{A} - \mathbf{B})\mathbf{cT} - \mathbf{bS}\omega_I] + \Delta[(\mathbf{A} + \mathbf{B})\mathbf{bS} - \mathbf{cT}\omega_I]}{\omega_I^2 - \Delta^2} \quad (12a)$$

$$\delta\mathbf{c}_I = \frac{\Delta[(\mathbf{A} - \mathbf{B})\mathbf{cT} - \mathbf{bS}\omega_I] + \omega_I[(\mathbf{A} + \mathbf{B})\mathbf{bS} - \mathbf{cT}\omega_I]}{\omega_I^2 - \Delta^2} \quad (12b)$$

The most time-consuming process in the algorithm is the application of the RPA operations  $\mathbf{A} + \mathbf{B}$  and  $\mathbf{A} - \mathbf{B}$  on the  $\mathbf{b}$  and  $\mathbf{c}$  vectors. This process can be accomplished through the generation of symmetric and antisymmetric Fock matrices followed by a projection onto particle–hole space. In computationally intense cases such as large molecules or extensive basis set calculations, integral evaluation in the Fock-matrix-generation step is the dominant component of the total CPU demand. The algorithmic details for obtaining  $m$  RPA roots are given in the following series of steps.

1. Choose  $l = l_{\text{initial}}$  trial bi-orthonormal vectors  $\mathbf{b}$  and  $\mathbf{c}$  (where  $l_{\text{initial}} > m$ ) representing approximate solutions. The dimension of the subspace spanned by  $\mathbf{b}$  and  $\mathbf{c}$  is  $L = l$ .

2. Create  $l$  symmetric and antisymmetric density matrices.

3. Generate  $l$  symmetric and antisymmetric Fock matrices and project them onto particle–hole space to obtain  $(\mathbf{A} + \mathbf{B})\mathbf{b}$  and  $(\mathbf{A} - \mathbf{B})\mathbf{c}$ .

4. Create effective Hamiltonians  $\mathbf{G}^S$  and  $\mathbf{G}^A$  for symmetric and antisymmetric modes by back projecting the Fock matrices onto the space spanned by the  $\mathbf{b}$  and  $\mathbf{c}$  vectors (dimension  $L$ ).

5. Solve the coupled equations of dimension  $L$  by a series of transformations in eq 8 to obtain  $\mathbf{S}$ ,  $\mathbf{T}$ , and  $\omega$ .

6. Generate  $m$  new pairs of error vectors  $\delta\mathbf{b}$  and  $\delta\mathbf{c}$  from eq 12.

7. Schmidt bi-orthonormalize, and append the new  $\mathbf{b}$  and  $\mathbf{c}$  vectors, with norms bigger than a certain threshold, to a set of previous vectors. Increment the size of the subspace  $L$  to  $L + l$  (where  $l \leq m$ ).

8. Go to step 2, and iterate the process until the norm of new error vectors  $\mathbf{b}$  and  $\mathbf{c}$  in step 6 or 7 becomes smaller than a certain threshold.

Alternatively, we can choose a set of orthonormal vectors  $\mathbf{b}$  to fulfill eq 6. The condition for the error vectors in this case becomes

$$\delta \mathbf{b}_l = \frac{(\mathbf{A} - \mathbf{B})\mathbf{b}\mathbf{T} - \mathbf{b}\mathbf{S}\omega_l}{\omega_l - \Delta} \quad (13a)$$

$$\delta \mathbf{b}_l = \frac{(\mathbf{A} + \mathbf{B})\mathbf{b}\mathbf{S} - \mathbf{b}\mathbf{T}\omega_l}{\omega_l - \Delta} \quad (13b)$$

The algorithm is similar to the case described above when  $\mathbf{c}$  is replaced by  $\mathbf{b}$ . In this case, however, we increment the subspace in step 7 by  $l'$  ( $l' \leq 2m$ ) spanned by the orthonormal vectors  $\mathbf{b}$ , which are obtained after Schmidt orthonormalization. Therefore, the dimension of the subspaces tends to increase twice as fast.

## Results and Discussion

We implemented the direct integral-driven RPA algorithm described above using both bi-orthonormal (case A) and orthonormal (case B) sets of error vectors. The preliminary application of the algorithm to an ethylene molecule with a small basis set (Table 1) indicates that both schemes provide monotonic convergence of the lowest five roots.

The lowest roots in case A require more iterations than those in case B, although the size of the final subspace is similar. Olsen et al. introduced a direct scheme in which the RPA problem is solved in a subspace via paired expansion vectors.<sup>6</sup> That algorithm provides fast convergence, but it requires a one-index transformation of integrals. Weiss et al.<sup>8</sup> and Ochsenfeld et al.<sup>9</sup> used a scheme in which  $(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})\mathbf{X} = \mathbf{X}\mathbf{W}$  is solved by consecutive operations on  $\mathbf{X}$ . Zakrzewski et al. implemented a direct RPA approach based on an algorithm in which eq 4 is directly projected onto a subspace spanned by error vectors to  $\mathbf{Z}$  and  $\mathbf{Y}$ .<sup>12</sup> However, they used symmetric and antisymmetric RPA operations in order to maximize the RPA operation per each integral-evaluation call (minimize the integral-evaluation calls per iteration). Therefore, the efficiency for this part of their algorithm should be similar to our implementation. In their implementation, the error vectors are generated by a denominator with the full diagonal element of the Hamiltonian, as in the original Davidson scheme.<sup>15</sup> The coupling nature of the oscillating amplitudes in the transition densities leads to a form of the equation in the time-dependent density functional theory (TDDFT) parallel to the one in the RPA equation. Recently, Stratmann et al. presented an implementation of the direct TDDFT.<sup>13</sup> In their algorithm, a set of coupled equations corresponding to eq 6 is solved directly. Indeed, the idea to work on the coupled equations goes far back to that of Tamura and Udagawa.<sup>14</sup> Stratmann et al. expanded the error vectors with a set of orthonormal vectors representing a subspace in which the projected equation is solved. This implementation seems similar to case B, although in our implementation, the bi-orthonormal condition (eq 7) is automatically guaranteed through a series of transformations (eq 8). The RPA equation has a paired solution giving a norm of identity and of minus identity. In the algorithm proposed by Olsen et al., the solutions are efficiently sought in the restricted subspace spanned by a pair of expansion vectors. In the present algorithm, the expansion vectors that are determined automatically fulfill bi-orthonormality (eq 7) except for the sign. The subspace is restricted to the correct one by appropriately choosing expansion vectors with a positive norm during the iteration. Furthermore, in method B, error vectors are chosen in a fashion reflecting the paired structure of the equation in order to increment the subspace with this restriction (eq 13).

As is noted above, the partition of the Hamiltonians in eq 11 is arbitrary, and the full set of diagonal elements are chosen in the denominator of the error vector in the original Davidson

**TABLE 1: Convergence in the Five Lowest Singlet–Singlet RPA Excitation Energies of Ethylene with a DZ Basis Set<sup>25</sup>**

| iteration   | A                              |                        | B                              |                        |
|-------------|--------------------------------|------------------------|--------------------------------|------------------------|
|             | energy difference <sup>a</sup> | dimension of subspaces | energy difference <sup>a</sup> | dimension of subspaces |
| First Root  |                                |                        |                                |                        |
| 1           | 35.05428                       | 10                     | 35.05448                       | 10                     |
| 2           | 3.63620                        | 15                     | 1.08381                        | 29                     |
| 3           | 0.70627                        | 20                     | 0.03408                        | 36                     |
| 4           | 0.55176                        | 25                     | 0.00113                        | 40                     |
| 5           | 0.21847                        | 29                     | 0.00002                        | 42                     |
| 6           | 0.17508                        | 33                     | 0.00000                        | 44                     |
| 7           | 0.07418                        | 35                     |                                |                        |
| 8           | 0.04283                        | 37                     |                                |                        |
| 9           | 0.01195                        | 39                     |                                |                        |
| 10          | 0.00821                        | 40                     |                                |                        |
| 11          | 0.00244                        | 41                     |                                |                        |
| 12          | 0.00102                        | 42                     |                                |                        |
| 13          | 0.00032                        | 43                     |                                |                        |
| 14          | 0.00022                        | 44                     |                                |                        |
| 15          | 0.00005                        | 45                     |                                |                        |
| 16          | 0.00002                        | 46                     |                                |                        |
| 17          | 0.00000                        | 47                     |                                |                        |
| Second Root |                                |                        |                                |                        |
| 1           | 8.70838                        | 10                     | 8.70838                        | 10                     |
| 2           | 0.32768                        | 15                     | 0.09622                        | 20                     |
| 3           | 0.04397                        | 20                     | 0.00000                        | 29                     |
| 4           | 0.00000                        | 25                     |                                |                        |
| Third Root  |                                |                        |                                |                        |
| 1           | 7.73479                        | 10                     | 7.73480                        | 10                     |
| 2           | 0.49870                        | 15                     | 0.09406                        | 20                     |
| 3           | 0.12671                        | 20                     | 0.00001                        | 29                     |
| 4           | 0.01487                        | 25                     | 0.00000                        | 36                     |
| 5           | 0.00015                        | 29                     |                                |                        |
| 6           | 0.00000                        | 33                     |                                |                        |
| Fourth Root |                                |                        |                                |                        |
| 1           | 4.71482                        | 10                     | 4.71489                        | 10                     |
| 2           | 0.39177                        | 15                     | 0.07437                        | 20                     |
| 3           | 0.26678                        | 20                     | 0.00104                        | 29                     |
| 4           | 0.04920                        | 25                     | 0.00000                        | 36                     |
| 5           | 0.01463                        | 29                     |                                |                        |
| 6           | 0.00206                        | 33                     |                                |                        |
| 7           | 0.00042                        | 35                     |                                |                        |
| 8           | 0.00011                        | 37                     |                                |                        |
| 9           | 0.00000                        | 39                     |                                |                        |
| Fifth Root  |                                |                        |                                |                        |
| 1           | 20.84438                       | 10                     | 20.84438                       | 10                     |
| 2           | 1.54166                        | 15                     | 0.07199                        | 20                     |
| 3           | 0.10884                        | 20                     | 0.00002                        | 29                     |
| 4           | 0.03919                        | 25                     | 0.00000                        | 36                     |
| 5           | 0.00012                        | 29                     |                                |                        |
| 6           | 0.00000                        | 33                     |                                |                        |

<sup>a</sup> The energy difference values (in 1000 au) are the differences from the final converged values.

scheme.<sup>15</sup> We partition the Hamiltonian with the zeroth-order HF manifold. The resulting denominator shift is a simple difference of HF eigenvalues. In the current implementation, the HF problem is solved before the RPA part begins, and the difference  $\Delta$  is a simple constant in the RPA iteration. The full set of diagonal elements contains the self-interaction of quasi-particles representing the particle–hole and hole–particle states, and the evaluation of the self-interaction term requires extra transformation of integrals. In direct implementations, such transformation should be avoided as much as possible. The most time-consuming process is the RPA operation on the error vectors. In the present implementation, the RPA operation is consistently interpreted as contraction of the two-body interaction  $V_N$  with the transition density matrices  $\bar{\rho}(r, r')$  of the symmetric and antisymmetric modes representing the quasi

**TABLE 2: Relative Timing of the RPA Iteration for the Five Lowest Roots of *trans*-Butadiene with the DH Basis Set<sup>26,a</sup>**

| iteration | dimension of subspaces | relative timing <sup>b</sup> |
|-----------|------------------------|------------------------------|
| 1         | 20                     | 3.815                        |
| 2         | 30                     | 3.815                        |
| 3         | 40                     | 3.813                        |
| 4         | 50                     | 3.817                        |
| 5         | 60                     | 3.821                        |
| 6         | 70                     | 3.823                        |
| 7         | 80                     | 3.826                        |
| 8         | 90                     | 3.830                        |
| 9         | 100                    | 3.833                        |

<sup>a</sup> C, [3S2P1D]; H, [2S1P]. Number of basis functions, 90; number of electrons, 30; number of particle–hole pairs, 1125. <sup>b</sup> Timing relative to a SCF cycle.

**TABLE 3: Relative Timing of the RPA Iteration for the Five Lowest Roots of C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>O with the STO-3G Basis Set<sup>24,a</sup>**

| iteration | dimension of subspaces | relative timing <sup>b</sup> |
|-----------|------------------------|------------------------------|
| 1         | 20                     | 1.95                         |
| 2         | 30                     | 1.95                         |
| 3         | 40                     | 1.96                         |
| 4         | 50                     | 1.96                         |
| 5         | 60                     | 1.96                         |
| 6         | 70                     | 1.97                         |
| 7         | 80                     | 1.97                         |
| 8         | 88                     | 1.97                         |
| 9         | 94                     | 1.67                         |
| 10        | 98                     | 1.46                         |

<sup>a</sup> Number of basis functions, 132; number of electrons, 160; number of particle–hole pairs, 4160. <sup>b</sup> Timing relative to a SCF cycle.

**TABLE 4: Relative Timing of the RPA Iteration for the Five Lowest Roots of Ethylene with the ANO Basis Set<sup>27,a</sup>**

| iteration | dimension of subspaces | relative timing <sup>b</sup> |
|-----------|------------------------|------------------------------|
| 1         | 20                     | 1.008                        |
| 2         | 30                     | 1.007                        |
| 3         | 40                     | 1.004                        |
| 4         | 49                     | 1.012                        |
| 5         | 57                     | 1.019                        |
| 6         | 65                     | 1.015                        |

<sup>a</sup> C, [14S9P/4S3P]; H, [8S/2S]. Number of basis functions, 34; number of electrons, 16; number of particle–hole pairs, 208. <sup>b</sup> Timing relative to a SCF cycle.

particles. Therefore, we can employ the same strategies as in the standard SCF theory, in which Fock matrix formation is nothing but the contraction of the two-body interaction with the zeroth-order density matrix. This part, corresponding to the RPA operations, is completely analogous to the perturbed Fock

matrix generation in the time-dependent Hartree–Fock (TDHF) theory for dynamic property evaluation.<sup>16</sup> In Tables 2–4, the relative timing of the RPA iteration for the lowest five singlet–singlet transitions compared to a SCF cycle, is shown. Method B is used for all of the examples.

In small molecule applications (Table 2), the ratio of the timing is a few times larger than unity, and the RPA computation consequently costs more than the SCF computation. However, in larger molecules (Table 3) or in cases with more extensive basis sets (Table 4), the ratio becomes close to unity, and the RPA computation costs less than the SCF computation. Note that the convergence criteria for those cases (Tables 2–4) is much more severe (a threshold of  $10^{-5}$  in the maximum norm of error vectors) than would be used in practice. The convergence in energy with a precision comparable to experiment could be obtained much more easily.

The efficiency of the algorithm depends on the convergence of the iteration and on the timing of the RPA operations in the iteration. The former depends on the application and the initial guesses, but the algorithm shows the efficient convergence property for the different applications examined here. For the latter, we can estimate the efficiency from the number of RPA operations that are performed for each iteration. In case A,  $l \leq m$ , the RPA operations for each symmetric and antisymmetric density matrix are performed, whereas  $l' \leq 2m$  RPA operations are required in case B. From this simple analysis, case A seems to be much more efficient than case B. In large molecules or in applications with an extended basis set, however, integral evaluation is much more time-consuming than the tracing of the integral with density matrices. The RPA operations ( $2l$  or  $2l'$  for symmetric and antisymmetric density matrices, respectively) in the present implementation are accomplished by a single evaluation of the complete set of integrals, accompanied by contractions with each transition density matrix, followed by a projection onto particle–hole and hole–particle spaces. The timing for each iteration is dominated by the single evaluation of the complete set of integrals. Therefore, the convergence property in the iteration is more important than the efficiency of the RPA operation in the iteration. From the data shown in Table 1, we feel that method B is more efficient than method A, especially for computationally demanding cases.

Although the error vector manifold consisting of **b** and **c** should be selected for particular excitations, the applications that we examined indicate that roots lying close together can be efficiently computed by a single manifold. In other words, a set of quasi particles is capable of describing several excited states.

As is seen in eq 11, we have made the simple choice for partitioning the Hamiltonians assuming the dominance of diagonal elements. Therefore, it should suffer from slow convergence problems, as in Davidson's scheme, in cases in

**TABLE 5: Convergence in the Five Lowest Singlet–Singlet RPA Excitation Energies of Benzene with the ANO Basis Set<sup>27,a</sup>**

| iteration | state          |                |                |                |                | dimension of subspaces | time (s) <sup>c</sup> |
|-----------|----------------|----------------|----------------|----------------|----------------|------------------------|-----------------------|
|           | 1 <sup>b</sup> | 2 <sup>b</sup> | 3 <sup>b</sup> | 4 <sup>b</sup> | 5 <sup>b</sup> |                        |                       |
| 1         | 4.71302        | 18.85071       | 31.37325       | 31.37327       | 16.92471       | 10                     | 394                   |
| 2         | 0.08134        | 0.22955        | 0.79194        | 0.79194        | 1.06073        | 20                     | 395                   |
| 3         | 0.00087        | 0.00484        | 0.03416        | 0.03416        | 0.13201        | 30                     | 395                   |
| 4         | 0.00001        | 0.00008        | 0.00237        | 0.00237        | 0.01951        | 40                     | 393                   |
| 5         | 0.00000        | 0.00001        | 0.00007        | 0.00006        | 0.00087        | 50                     | 395                   |
| 6         | 0.00000        | 0.00000        | 0.00000        | 0.00000        | 0.00007        | 60                     | 395                   |
| 7         | 0.00000        | 0.00000        | 0.00000        | 0.00000        | 0.00000        | 70                     | 395                   |

<sup>a</sup> C, [14S9P/3S2P]; H, [8S4P/2S1P]. Number of basis functions, 84; number of electrons, 42; number of particle–hole pairs, 1323. <sup>b</sup> The numbers (in 1000 au) are the differences from the final converged values. <sup>c</sup> Each SCF cycle took 331 s (14 510 s with GAMESS integrals) and required 15–16 iterations to converge. Each iteration in the RPA took about 14 670 s with GAMESS integrals.



which nondiagonal elements dominate. Improvement can be achieved by using different techniques, such as shifted inverse-power methods.<sup>17</sup> It is also possible to enhance the convergence property by separating the computation and executing the iterative scheme for each category in which the error vector manifold describes a single type of excitation. The characterization of the excitation is easily realized by back transforming the transition density matrices onto the physical space expressed by the basis set. The development of a more efficient implementation for general cases is in progress by taking the above concepts into consideration.

In the cases in which integral evaluation is not completely dominant, each RPA iteration takes longer than a SCF cycle, so the RPA computation takes more time than the SCF computation. However, in computationally more intense cases, such as with generally contracted basis sets (Tables 4 and 5), the time required for each RPA iteration is almost equivalent to that required for a SCF cycle, and consequently the RPA computation costs less than the SCF computation. For applications with larger molecules, we expect the same situation. In those cases, improvement in integral evaluation is a very important issue. We implemented the direct RPA scheme using integral-evaluation routines from SPHERICA,<sup>18</sup> as well as GAMESS.<sup>19</sup> The implementation is performed using Fortran 90 and Fortran 77 on both AIX (RS6000) and PC-Linux platforms. The integral evaluation in SPHERICA employs the accompanying coordinate expansion (ACE) formalism developed by Ishida<sup>20</sup> and outperforms considerably standard program packages such as HONDO<sup>21</sup> and Gaussian 98<sup>22</sup> in two-electron integral evaluation of generally contracted basis sets (from several times to a few orders of magnitude improvement).<sup>23</sup> The timings of a RPA iteration and a SCF cycle are compared using IBM/POWER3-260, and the results are shown in Table 5, together with the timings found using the GAMESS integral routines. The implementation with SPHERICA, when compared with the implementation using the GAMESS integral routines, reveals overwhelming efficiency for the generally contracted basis set applications. This performance superiority using SPHERICA was reported in more detail.<sup>28</sup> However, relative timing of the RPA computation compared to the SCF computation does not vary much between those two cases, indicating the efficiency of the algorithm employed. It must be noted, however, that the present algorithm is based on the projection of transition density matrices onto HF particle-hole and hole-particle spaces. This projection would cost more than the integral evaluation for applications with very large molecules in which the diminishing coulomb force can scale down the relative cost of the integral evaluations. An algorithm in which the transition density matrices are directly determined without projection is required for those cases, and the development of such an algorithm is in progress.<sup>29</sup>

## Conclusions

We developed a direct RPA algorithm in which the excited states are directly computed in terms of quasi particles fulfilling an equation of motion in particle-hole and hole-particle spaces. The direct integral-driven RPA is implemented using this scheme. The error vectors representing the quasi particles are expanded on the subspaces using a bi-orthonormal and/or an orthonormal set. The latter scheme seems to be better suited for computationally intensive applications. Several applications indicated the efficiency of the algorithm for the lowest excited states of molecules, and the RPA computation costs less than the SCF computation for computationally demanding cases. The

implementation with new integral-generation routines based on ACE reveals overwhelming performance superiority for applications using generally contracted basis sets.

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## References and Notes

- (1) Dunning, T. H.; MaKoy, V. J. *Chem. Phys.* **1967**, *47*, 1735.
- (2) Oddershede, J. *Adv. Chem. Phys.* **1987**, *69* (II), 201.
- (3) Linderberg, J.; Öhrn, Y. *Propagator in Quantum Chemistry*; Academic Press: New York, 1973.
- (4) Rettrup, S. *J. Comput. Phys.* **1982**, *45*, 100.
- (5) Bouman, T. D.; Hansen, A. E.; Voigt, B.; Rettrup, S. *Int. J. Quantum Chem.* **1983**, *23*, 595.
- (6) Olsen, J.; Aa Jensen, H. J.; Jørgensen, P. *J. Comput. Phys.* **1988**, *74*, 265.
- (7) Narita, S.; Shibuya, T. *Can. J. Chem.* **1992**, *70*, 296 (special issue for Huzinaga).
- (8) Weiss, H.; Ahlrichs, R.; Häser, M. *J. Chem. Phys.* **1993**, *99*, 1262.
- (9) Ochsenfeld, C.; Gauss, J.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *103*, 7401.
- (10) Ågren, H.; Vahtras, O.; Koch, H.; Jørgensen, P.; Helgaker, T. *J. Chem. Phys.* **1993**, *98*, 6417.
- (11) Koch, H.; Ågren, H.; Jørgensen, P.; Helgaker, T.; Aa Jensen, H. *J. Chem. Phys.* **1993**, *172*, 13.
- (12) Zakrzewski, V. G.; Dolgounitcheva, O.; Ortiz, J. V. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1996**, *30*, 29.
- (13) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218.
- (14) Tamura, T.; Udagawa, T. *Nucl. Phys.* **1964**, *53*, 33.
- (15) Davidson, E. R. *J. Comput. Phys.* **1975**, *17*, 87.
- (16) Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *85*, 976.
- (17) Strang, G. *Linear Algebra and its Applications*; Academic Press: New York, 1976.
- (18) SPHERICA is an ab initio quantum chemical program package developed mainly by T. Yanai in Prof. K. Hirao's laboratory at the University of Tokyo.
- (19) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347-1363 (GAMESS).
- (20) Ishida, K. *J. Chem. Phys.* **1993**, *98*, 2176; *Int. J. Quantum Chem.* **1995**, *59*, 209.
- (21) Dupuis, M.; Marquez, A.; Davidson, E. R. *HONDO 95.6*; IBM Corporation: Kingston, NY, 1995.
- (22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (23) Yanai, T.; Ishida, K.; Nakano, H.; Hirao, K. *Int. J. Quantum Chem.* In press (special issue for the anniversary of Rudenberg).
- (24) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657-2664 (STO-3G).
- (25) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823 (double zeta).
- (26) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Shafer, H. F., III, Ed.; Plenum Press: New York, 1977; pp 1-27 (Dunning Hay).
- (27) Widmark, P. O.; Malmqvist, P. A.; Roos, B. O. *Theor. Chim. Acta* **1991**, *77*, 291 (atomic natural orbital).
- (28) Sekino, H.; Yanai, T.; Hirao, K. *Nonlinear Optics*; Gordon and Breach Science Publishers: Takarazuka, Japan, in press (special issue for the International Workshop on Molecular Design of Photonic Materials).
- (29) To be published.