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A cubic scaling algorithm for excited states calculations in particle–particle random phase approximation ☆

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ABSTRACT

The particle–particle random phase approximation (pp-RPA) has been shown to be capable of describing double, Rydberg, and charge transfer excitations, for which the conventional time-dependent density functional theory (TDDFT) might not be suitable. It is thus desirable to reduce the computational cost of pp-RPA so that it can be efficiently applied to larger molecules and even solids. This paper introduces an $O(N^3)$ algorithm, where N is the number of orbitals, based on an interpolative separable density fitting technique and the Jacobi–Davidson eigensolver to calculate a few low-lying excitations in the pp-RPA framework. The size of the pp-RPA matrix can also be reduced by keeping only a small portion of orbitals with orbital energy close to the Fermi energy. This reduced system leads to a smaller prefactor of the cubic scaling algorithm, while keeping the accuracy for the low-lying excitation energies.

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1. Introduction

While the time-dependent density functional theory (TDDFT) [1,12] has been widely used in the prediction of electronic excited states in large systems because of its low computational cost and satisfying accuracy, it is known however that TDDFT is not able to well describe double, Rydberg, charge transfer, and extended π-systems excitations [2], which limits its applications in many practical problems. This motivates the development of the particle–particle random phase approximation (pp-RPA) [9,14,18] for excited state calculations. It has been shown that the pp-RPA gives quite accurate prediction of electronic excited states in moderate size molecular systems [10,20].

However, the application of the pp-RPA is still limited to small size systems due to its expensive computational cost. Suppose N is the size of a given Hamiltonian after discretization, a naive implementation takes $O(N^6)$ operations to solve the pp-RPA equation, where N is the number of orbitals. Recently, [20] proposed an $O(N^4)$ algorithm that is comparable with other commonly used methods, e.g., configuration interaction singles (CIS) and TDDFT methods. To make the application of the pp-RPA feasible to larger systems, this paper proposes an $O(NN_{\mathrm{aux}}^2 + N^2N_{\mathrm{aux}} + N^2N_{\mathrm{grid}})$ algorithm based on a newly developed technique, the interpolative separable density fitting in [6,7]. Here N_{aux} is the number of auxiliary basis functions used in the density fitting and N_{grid} is the total number of real space grid points, both scale linearly with N, and hence the overall scaling of the proposed algorithm is $O(N^3)$.

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In the numerical linear algebra point of view, the excited states calculation in pp-RPA amounts to solving a generalized eigenvalue problem. When focusing on low-lying excitations, the smallest (in terms of the magnitude) few eigenpairs are desired. We refer the readers to [10] for the formal derivation of the pp-RPA theory.

To simplify the discussion, let us consider systems in the domain with periodic boundary condition, and without loss of generality, assumed to be $\mathbb{T} = [0,1]^d$. After discretization (such as the pseudo-spectral method employed in our numerical examples), the number of total spatial grid points is denoted by N_{grid}. Thus the Hamiltonian operator H becomes an $N_{\text{grid}} \times N_{\text{grid}}$ real symmetric matrix. $\{(\epsilon_p, \phi_p)\}_{p=1,\ldots,N_{\text{grid}}}$ denote the N_{grid} eigenpairs of H:

$$H\phi_p = \epsilon_p \phi_p, \qquad \forall\, p = 1, \ldots, N_{\text{grid}}. \tag{1}$$

The eigenvectors ϕ_p will be referred as orbitals and the associated eigenvalues as orbital energy. According to the Pauli's exclusion principle, the low-lying eigenstates are occupied. The number of occupied orbitals is denoted by N_{occ} (throughout this work, we assume that the N_{occ}-th eigenvalue is non-degenerate, i.e., $\epsilon_{N_{\text{occ}}} < \epsilon_{N_{\text{occ}}+1}$). The rest of the orbitals are virtual ones (also known as unoccupied orbitals). The virtual orbitals have higher orbital energy than the occupied ones; the eigenvalues are separated by the Fermi energy:

$$\epsilon_F = \frac{1}{2}\left(\epsilon_{N_{\text{occ}}} + \epsilon_{N_{\text{occ}}+1}\right). \tag{2}$$

Therefore, the occupied orbitals have energy less than the Fermi energy while the virtual ones have energy higher than ϵ_F.

We follow the convention of quantum chemistry literature to use indices i, j, k, and l to index occupied orbitals, a, b, c, and d for virtual orbitals, and p, q, r, and s for unspecified orbitals. Assume that we consider the first N_{vir} virtual orbitals (ordered by eigenvalues) and $N = N_{\text{occ}} + N_{\text{vir}}$ denotes the total number of orbitals under consideration, the generalized eigenvalue problem of pp-RPA is given by

$$\begin{pmatrix} A & B \\ B^\top & C \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} I_p & \\ & -I_h \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}, \tag{3}$$

where I_p and I_h are identity matrices of dimension $N_p = \binom{N_{\text{occ}}}{2}$ and $N_h = \binom{N_{\text{vir}}}{2}$, respectively, and entries in matrices A, B, and C are defined via

$$\begin{aligned} A_{ijkl} &= \langle ij||kl\rangle + \delta_{ik}\delta_{jl}(\epsilon_i + \epsilon_j - 2\epsilon_F), \\ B_{ijcd} &= \langle ij||cd\rangle, \\ C_{abcd} &= \langle ab||cd\rangle - \delta_{ac}\delta_{bd}(\epsilon_a + \epsilon_b - 2\epsilon_F), \end{aligned}$$

for $1 \le j < i \le N_{\text{occ}}$, $1 \le l < k \le N_{\text{occ}}$, $N_{\text{occ}} + 1 \le b < a \le N$, and $N_{\text{occ}} + 1 \le d < c \le N$, where

$$\langle pq||rs\rangle = \langle pq \mid rs\rangle - \langle pq \mid sr\rangle,$$

and

$$\langle pq \mid rs\rangle = \iint\limits_{\mathbb{T}\times\mathbb{T}} \phi_p(r_1)\phi_q(r_2)\phi_r(r_1)\phi_s(r_2) v_c(r_1 - r_2)\, \mathrm{d}r_1\, \mathrm{d}r_2$$

is the four-center two-electron repulsion integral. Here $v_c(\cdot)$ is the periodic Coulomb kernel (due to our choice of the periodic boundary condition) given by the fundamental solution of the Poisson equation with a periodic boundary condition on $\mathbb{T}$:

$$-\Delta v_c(\cdot) = 4\pi(\delta(\cdot) - 1), \tag{4}$$

where $\delta(\cdot)$ is the Dirac delta function.

The dimension of pp-RPA matrix

$$\begin{pmatrix} A & B \\ B^\top & C \end{pmatrix} \tag{5}$$

is $O(N^2) \times O(N^2)$; and thus constructing the whole pp-RPA matrix takes at least $O(N^4)$ operations, since it contains $O(N^4)$ entries. The action of this matrix to a vector also scales as $O(N^4)$ in general. Thus, the standard approach for the generalized eigenvalue problem (3) has a computational cost at least $O(N^4)$ for getting a single eigenpair.

In this work, we propose an $O(N^3)$ scaling algorithm to obtain a few eigenpairs of the generalized eigenvalue problem above. The observation is that if an iterative algorithm such as the Jacobi–Davidson eigensolver [15,16] is used, the computational bottleneck is to apply the pp-RPA matrix to a vector (referred as matvec in the sequel); in particular, it is not necessary to construct the matrix for matvec. An $O(N^3)$ matvec is available by an efficient representation of the electron repulsion integral tensor enabled by the recently proposed interpolative separable density fitting in [6,7]. Combined with the Jacobi–Davidson iterative eigensolver, this gives a cubic scaling algorithm for the pp-RPA excitation energy calculation.

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