Accelerate stochastic calculation of random-phase approximation correlation energy difference with atom-based correlated sampling

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Introduction

A kernel polynomial method (KPM) is developed to calculate the random phase approximation (RPA) correlation energy. In this method, the RPA correlation energy is formulated in terms of the density of states (DOS) for the eigenvalues of the matrix obtained as the product between the Coulomb operator and Kohn-Sham (KS) linear response function. The integration over the eigenvalues is then calculated using KPM [1, 2]. Since energy differences between similar systems are of much interest in practice, we also develop a scheme, atom-based correlated sampling (ACS), to accelerate the convergence of energy-difference calculations. In the study, the KPM is used to calculate the isomerization energy between acetone and 2-propenol and ACS is used to accelerate the convergence of energy difference calculations. The KPM developed in this work, together with the ACS scheme, is expected to be useful for calculating RPA correlation energy difference between two systems that only differ in a local region, for example, calculation of adsorption energies of molecules for surface catalysis. For these types of calculations, the computational cost of our method scales quadratically with the system’s size.

Theoretical Methods

The RPA correlation energy within the adiabatic connection fluctuation-dissipation theorem (ACFDT) formalism is written as

$$E_{\text{RPA}} = \frac{1}{2} \int \sum \left[ u_i |(1 - \chi_0(r, r'; u_i)\chi_0(r, r'; u_i)] \right],$$  \hspace{1cm} (1)

where $u_i(r, r') = 1/|r-r'|$ is the Coulomb potential, $\chi_0(r, r'; u_i)$ is the KS linear response function at the imaginary frequency $u_i$ and can be explicitly expressed in terms of KS orbitals $(\phi_i(r))$, eigenvalues ($\epsilon_i$), and occupation numbers ($n_i$) as

$$\chi_0(r, r'; u_i) = 2 \sum_j \sum_k (f_i - f_k) \phi_i(r) \phi_j(r') \phi_k(r) \phi_k(r') / \epsilon_j - \epsilon_k + u_i.$$  \hspace{1cm} (2)

where indices $j$ and $k$ loop over all the KS orbitals. Due to the fact the trace is invariant under cyclic permutations, $\chi_0(r, r')$ in Eq. 1 can be replaced by $\psi_1^{\text{RPA}} \psi_2^{\text{RPA}} / \sqrt{\sigma_r}$. Which is denoted by $\mathcal{M}$ in this work, that is, $\mathcal{M} = \psi_1^{\text{RPA}} / \sqrt{\sigma_r}$. To formulate the correlation energy using KPM, the RPA correlation energy becomes

$$E_{\text{RPA}} = \frac{1}{2\pi^2} \int_0^\infty \int d\epsilon d\epsilon' \left[ g_{\epsilon,\epsilon'} + 2 \sum_{\ell=1}^{N_{\text{RPA}}} g_{\epsilon,\epsilon'} c_{\ell} c_{\ell} \right],$$  \hspace{1cm} (3)

$\mathcal{T}_s$ is the $s$-th order Chebyshev polynomial and $g_{\epsilon,\epsilon'}$ is the atom kernels. $c_{\ell}$ is defined as

$$c_{\ell} = \int (\sqrt{\epsilon} \mathcal{T}_s(\epsilon') / \int \phi_i(\epsilon') / (\epsilon - \epsilon_i + u_i)^2$$  \hspace{1cm} (4)

\hspace{2cm} where $T_s(\epsilon)$ is the $s$-th order Chebyshev polynomial and $g_{\epsilon,\epsilon'}$ is given by the trace of $\mathcal{T}_s(\mathcal{T}_s(\epsilon) \mathcal{T}_s(\epsilon'))$.  \hspace{1cm} (5)

where $\mathcal{M}$ is the rescale spectrum of the $\mathcal{M}$ that its eigenvalues are inside $(-1, 1)$. The RPA energy difference is

$$\Delta E_{\text{RPA}} = E_{\text{RPA}}(\text{acetone}) - E_{\text{RPA}}(\text{2-propenol}),$$  \hspace{1cm} (6)

where $E_{\text{RPA}}$ and $\Delta E_{\text{RPA}}$ are the RPA correlation energies of the system 1 and the system 2, respectively. In the ACS scheme, we calculate the RPA correlation contribution to the atomization energy (AE) as

$$E_{\text{RPA}}^{\text{AE}} = E_{\text{RPA}}^{\text{AE}_1} - E_{\text{RPA}}^{\text{AE}_2},$$  \hspace{1cm} (7)

where $E_{\text{RPA}}^{\text{AE}}$ and $\Delta E_{\text{RPA}}^{\text{AE}}$ are the RPA correlation energies of the 1 and the 2 atom systems, respectively.

Results

The performance of RPA-KPM (with and without using ACS) is investigated with the RPA correlation energy difference for the isomerization of acetone to 2-propenol. Figure 1 shows that isomerization of (a) acetone to (b) 2-propenol by transferring H6. In this example, acetone is treated as the system 1 and 2-propenol is treated as the system 2.

In Figure 2, we show the performance of RPA-KPM with respect to different number of random vectors for this two similar systems. The benchmarks are obtained by calculating the RPA correlation energies using conjugate gradient method [4]. The performance of RPA-KPM with and without using ACS is demonstrated in Figure 2 (a), which shows the convergence of $\Delta E_{\text{RPA}}$ with respect to the number of random vectors. 50 moments are used in the calculations. The standard errors are denoted by the red and blue bands. Using ACS, RPA-KPM’s results stay closer to the benchmark and have smaller standard errors.

Summary and Outlook

In this work, we have developed a kernel polynomial method to calculate the RPA correlation energy. We focused on calculating the RPA correlation energy difference between two similar systems, which is of much interest in practice. In order to accelerate the convergence of energy-difference calculations, we have developed the atom-based correlated sampling method to accelerate the convergence of energy difference calculations. The convergence of this example is much accelerated by ACS with a boost factor of 3.6. The above results have been published in Electronic Structure [5].

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References