

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-propanol 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

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty du \text{Tr}[\ln(1 - \chi_0(\mathbf{r}, \mathbf{r}'; iu)v_c) + \chi_0(\mathbf{r}, \mathbf{r}'; iu)v_c], \quad (1)$$

where $v_c(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ is the Coulomb potential. $\chi_0(\mathbf{r}, \mathbf{r}'; iu)$ is the KS linear response function at the imaginary frequency iu and can be explicitly expressed in term of KS orbitals ($\{\phi_j(\mathbf{r})\}$), eigenvalues ($\{\epsilon_j\}$), and occupation numbers ($\{f_j\}$) as

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = 2 \sum_j \sum_k (f_j - f_k) \frac{\phi_j^*(\mathbf{r})\phi_k(\mathbf{r}')\phi_k^*(\mathbf{r}')\phi_j(\mathbf{r})}{\epsilon_j - \epsilon_k + iu}, \quad (2)$$

where indices j and k loop over all the KS orbitals. Due to the fact the trace is invariant under cyclic permutations, $\chi_0 v_c$ in Eq. 1 can be replaced by $v_c^{1/2} \chi_0 v_c^{1/2}$, which is denoted by M in this work, that is, $M(iu) = v_c^{1/2} \chi_0(iu) v_c^{1/2}$. To formulate the RPA correlation energy using KPM, the RPA correlation energy becomes

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty du \left[g_0 c_0 \mu_0 + 2 \sum_{n=1}^\infty g_n c_n \mu_n \right], \quad (3)$$

T_n is the n -th order Chebyshev polynomial and $\{g_n\}$ are the Jackson kernels. c_n is defined as

$$c_n = \int_{-1}^1 \frac{1}{\pi \sqrt{1-x^2}} T_n(\tilde{x}) [\ln(1 - (a\tilde{x} + b)) + (a\tilde{x} + b)] d\tilde{x}. \quad (4)$$

$\{\mu_n\}$ are given by the trace of $\text{Tr}[T_n(\tilde{M})]$

$$\mu_n = \text{Tr}[T_n(\tilde{M})] \approx \frac{1}{R} \sum_{r=1}^{R-1} \langle r | T_n(\tilde{M}) | r \rangle. \quad (5)$$

Here $|r\rangle$ is a normal random numbers with zero mean and unit variance[1, 3]. To compute the product of $T_n(\tilde{M})$ and $|r\rangle$, we use the three-term recurrence relation of Chebyshev polynomials

$$T_n(\tilde{M}) |r\rangle = 2\tilde{M} T_{n-1}(\tilde{M}) |r\rangle - T_{n-2}(\tilde{M}) |r\rangle, \quad (6)$$

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

$$\Delta E_c^{RPA} = E_{c1}^{RPA} - E_{c2}^{RPA}, \quad (7)$$

where E_{c1}^{RPA} and E_{c2}^{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

$$E_{AE,1}^{RPA} = E_{c1}^{RPA} - \sum_{i=1}^{N_{\text{atom}}} E_{c1, \text{atom}_i}^{RPA} \quad (8)$$

$$E_{AE,2}^{RPA} = E_{c2}^{RPA} - \sum_{i=1}^{N_{\text{atom}}} E_{c2, \text{atom}_i}^{RPA}, \quad (9)$$

where i runs over all the atoms in each system and N_{atom} is the number of atoms. $E_{c1, \text{atom}_i}^{RPA}$ and $E_{c2, \text{atom}_i}^{RPA}$ are the atom i 's RPA correlation energies calculated using RPA-KPM, as described above. The RPA correlation energy difference between the two systems is then calculated as

$$\Delta E_{c, \text{ACS}}^{RPA} = E_{AE,1}^{RPA} - E_{AE,2}^{RPA}. \quad (10)$$

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-propanol. Figure 1 shows that isomerization of (a) acetone to (b) 2-propanol by transferring H6. In this example, acetone is treated as the system 1 and 2-propanol is treated as the system 2.

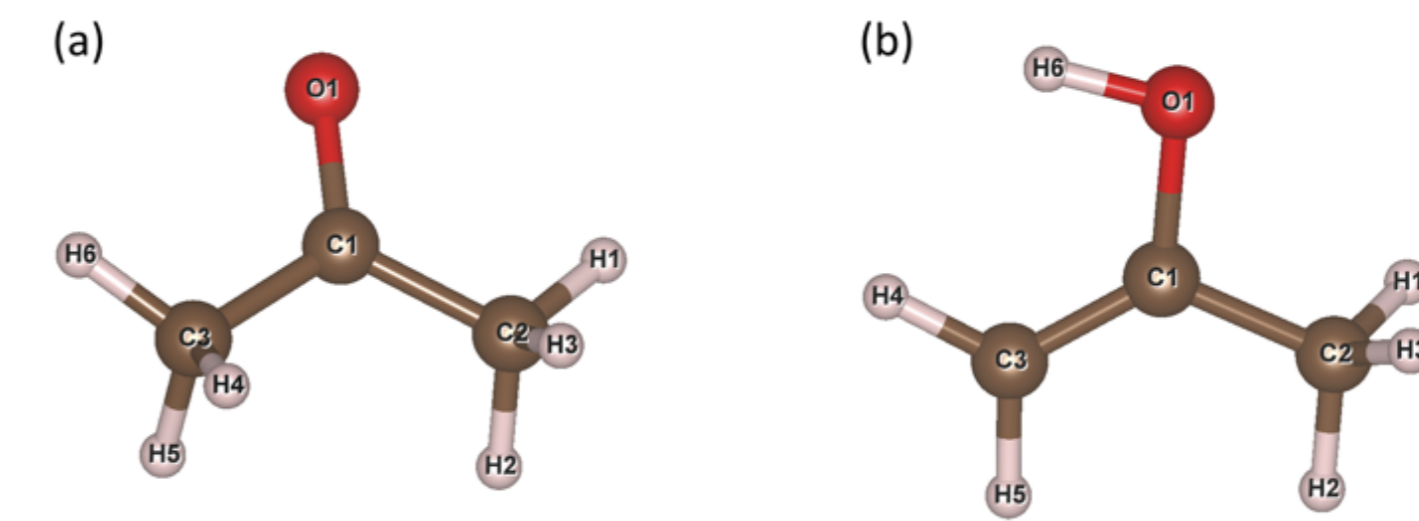


Figure 1: Isomerization of (a) acetone to (b) 2-propanol by transferring H6. The oxygen, carbon, hydrogen atoms are red, brown, and grey, respectively.

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 ΔE_c^{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.

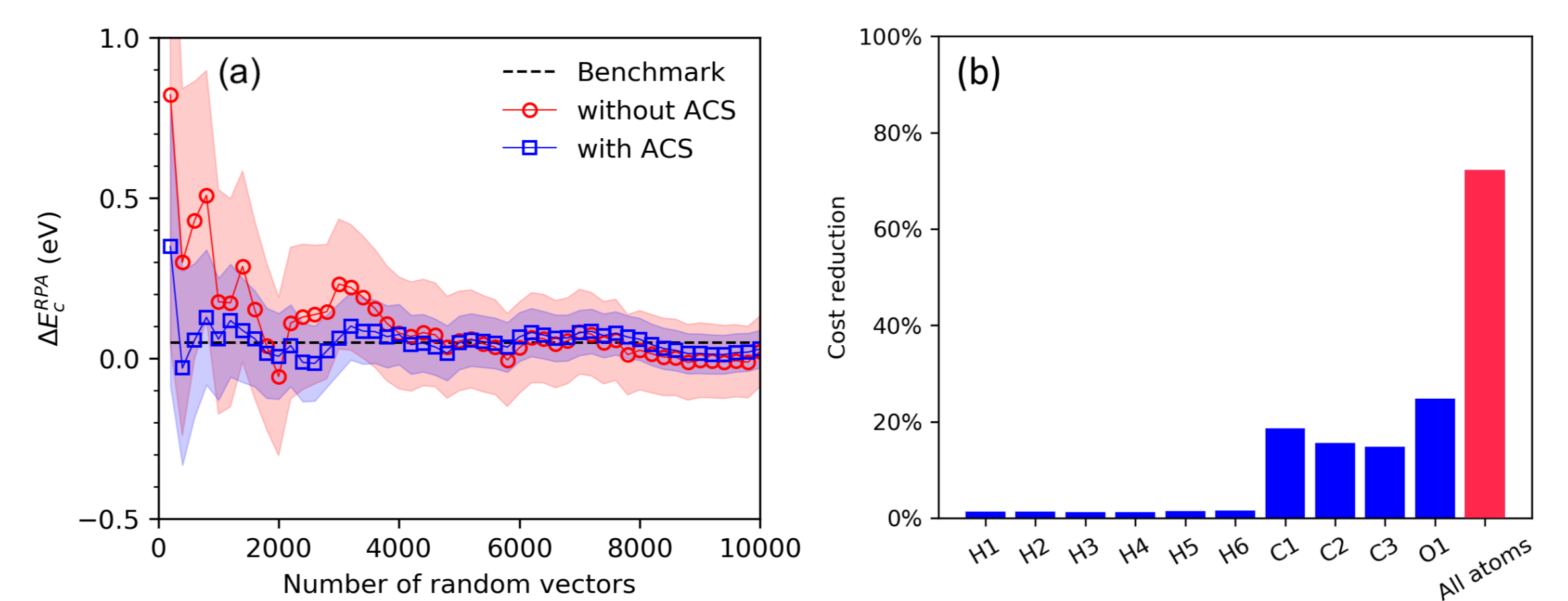


Figure 2: (a) Convergence of the RPA correlation energy difference between acetone and 2-propanol with respect to the number of random vectors, calculated with and without ACS. Standard errors are represented by the red and blue bands. Benchmark is denoted by the dashed line. (b) Cost reduction for applying ACS to each and to all the atoms. 50 moments are used.

The goal of ACS is to reduce the standard error from sampling ΔE_c^{RPA} , which in turn reduces the number of random vectors. Due to the central limit theorem, standard error decreases as $1/\sqrt{R}$, where R is the number of random vectors. The cost reduction (q) is then related to the standard error as

$$q = 1 - \left(\frac{\sigma_{\text{err}}^{\text{ACS}}}{\sigma_{\text{err}}} \right)^2, \quad (11)$$

where $\sigma_{\text{err}}^{\text{ACS}}$ and σ_{err} are the standard errors for $\Delta E_{c, \text{ACS}}^{RPA}$ and ΔE_c^{RPA} , respectively. They are related to the variances as $\sigma_{\text{err}}^{\text{ACS}} = \frac{1}{R} \sqrt{\text{Var}(\Delta E_{c, \text{ACS}}^{RPA})}$ and $\sigma_{\text{err}} = \frac{1}{R} \sqrt{\text{Var}(\Delta E_c^{RPA})}$. The cost reduction due to ACS is 72% (labeled by "All atoms" in Figure 2(b)). This corresponds to an acceleration of 3.6. In other words, for a fixed error in ΔE_c^{RPA} , the number of random vectors needed by RPA-KPM with using ACS is 3.6 times less than that needed by RPA-KPM without using ACS.

In order to examine each atom's contribution to the cost reduction, we performed ACS for each atom, separately. In Figure 2(b), the bar labeled by "H1" is obtained by applying ACS only to H1. It is observed that all H atoms do not contribute much to the cost reduction due to their small contribution to the total RPA correlation energy. Most of the cost reduction is from C and O atoms. The sum of all atomic cost reduction is 82%, which is larger than the "All atoms" reduction (72%). This is expected because samplings in the atomic regions are not fully decoupled.

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].

Acknowledgments

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