

Directly calculating the RPA correlation energy difference between two similar systems

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Introduction

Random Phase approximation (RPA) correlation provides a route to improve the accuracy of Kohn-Sham (KS) density functional theory (DFT). In our previous project, we developed an efficient stochastic method[1] to calculate the RPA correlation energy differences between two similar large systems. In this work, we implemented a method to calculate RPA correlation energy directly based on Ref. [2]. The RPA correlation energy can be formulated in terms of the trace of a large matrix. That matrix is the product between the Coulomb matrix and the KS linear response function. The trace is then expressed in terms of the eigenvalues of that large matrix. Fortunately, most of the eigenvalues are very close to zero and do not contribute much to the RPA correlation energy. We then develop a method to solve the lowest eigenvalues of this large matrix. The conjugate gradient (CG) method is used to solve for these low eigenvalues one by one. The Gram-Schmidt procedure is used to ensure that the current eigenvector is orthogonal to all lower eigenvectors[3]. This method allows us to calculate the RPA correlation energy by solving the lowest eigenvalues of the large matrix directly.

Theoretical Methods

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

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

where $\text{Tr}[AB] = \int \int d^3r d^3r' A(\mathbf{r}, \mathbf{r}') B(\mathbf{r}, \mathbf{r}')$. $\chi_0(iu)$ is the linear response function of the non-interacting electron system at frequency iu . v_c is the Coulomb interaction $v_c = 1/|\mathbf{r} - \mathbf{r}'|$. The RPA correlation energy can therefore be written in terms of the density of state (DOS) of the matrix $M = v_c^{1/2} \chi_0 v_c^{1/2}$ as

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty du \int_{-\infty}^0 \rho_M(x; iu) [\ln(1-x) + x] dx. \quad (2)$$

where x is the eigenvalue of M . The second integral's upper limit is 0 because the matrix M is semi-negative-definite. In order to employ the kernel polynomial method (KPM), we need to rescale $\tilde{M} = (M - b)/a$ to make its spectrum to fall within $(-1, 1)$. The RPA correlation energy can be written in terms of the DOS of the rescaled matrix \tilde{M} as

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty du \int_{-1}^1 \tilde{\rho}_{\tilde{M}}(\tilde{x}; iu) [\ln(1 - (a\tilde{x} + b)) + (a\tilde{x} + b)] d\tilde{x}, \quad (3)$$

where \tilde{x} is the eigenvalue of \tilde{M} . We define $\tilde{\rho}_{\tilde{M}}(\tilde{x}; u) = a \rho_M(\tilde{x}a + b; u)$ which is the DOS of \tilde{M} and is computed as

$$\tilde{\rho}_{\tilde{M}}(\tilde{x}) = \frac{1}{\pi \sqrt{1 - \tilde{x}^2}} \left[g_0 \mu_0 + 2 \sum_{n=1}^{\infty} g_n \mu_n T_n(\tilde{x}) \right], \quad (4)$$

where $\{g_n\}$ are the Jackson kernels to suppress the Gibbs oscillations. To determine $\tilde{\rho}_{\tilde{M}}(\tilde{x})$, we compute the moments $\{\mu_n\}$, which are given by $\text{Tr}[T_n(\tilde{M})]$.

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

Here $|r\rangle$ is a set of random vectors that satisfy $\langle \xi_{rj} \rangle = 0$ and $\langle \xi_{ri} \xi_{rj} \rangle = \delta_{rr'} \delta_{ij}$, where $\xi_{ri} \in \mathbf{R}$ denotes the i th element of a vector $|r\rangle$ and $\langle \dots \rangle$ denotes the statistical average with respect to different realizations of random vectors[4]. To compute the product of $T_n(\tilde{M})$ and $|r\rangle$, we use the three-term recurrence relation of the Chebyshev polynomials

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

The final expression for the RPA correlation energy in terms of the moments are

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty du \left[g_0 c_0 \mu_0 + 2 \sum_{n=1}^{\infty} g_n c_n \mu_n \right], \quad (7)$$

where c_n is defined as

$$c_n = \int_{-1}^1 \frac{1}{\pi \sqrt{1 - \tilde{x}^2}} T_n(\tilde{x}) [\ln(1 - (a\tilde{x} + b)) + (a\tilde{x} + b)] d\tilde{x}. \quad (8)$$

A different method to calculate E_c^{RPA} is to calculate the relatively small number of eigenvalues of $v_c^{1/2} \chi_0 v_c^{1/2}$.

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty du \sum_{\alpha=1}^N \{ \ln[1 - a_\alpha(iu)] + a_\alpha(iu) \}, \quad (9)$$

where the eigenvalues $a_\alpha(iu)$ and their corresponding eigenvectors ΔV_α are defined through the solution of the eigenvalue problem:

$$v_c^{1/2} \chi_0(iu) v_c^{1/2} |\Delta V_\alpha\rangle = a_\alpha |\Delta V_\alpha\rangle. \quad (10)$$

Conjugate Gradient Scheme

The CG scheme is used to evaluate the smallest eigenpairs, and the pseudocode of CG algorithm for finding smallest eigenpairs problem can be outlined as following.

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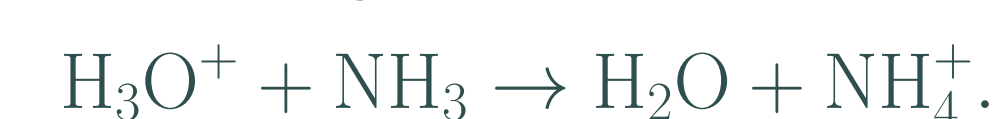
Initialization:  $\{|v_m\rangle\}$ 
Gram-Schmidt procedure:  $|v_m\rangle = |v_m\rangle - \sum_{i=1}^{m-1} \langle v_m | v_i \rangle |v_i\rangle$ 
foreach  $n = 1$  to  $niter$  do
  foreach  $m = 1$  to  $n_{eigen}$  do
    Let  $d_o = 0$ 
    foreach  $j = 1$  to  $n_{line}$  do
      Compute  $\lambda_m = \langle v_m | A | v_m \rangle / \langle v_m | v_m \rangle$ 
      if  $(\|Av_m - \lambda_m v_m\|_2 < tol)$  then
        exit
      end
    Compute the gradient  $g_j = \frac{2Av_m}{\langle v_m | v_m \rangle} - 2 \frac{\langle v_m | A | v_m \rangle}{\langle v_m | v_m \rangle^2} v_m$ , and perform Gram-Schmidt
    procedure  $|g_j\rangle = |g_j\rangle - \sum_{i=1}^{m-1} \langle g_j | v_i \rangle |v_i\rangle$ 
    Make the CG direction  $d_j = -g_j + \beta d_{j-1}$  with  $\beta = \frac{\langle g_j | g_{j-1} \rangle}{\langle g_{j-1} | g_{j-1} \rangle}$ 
     $v_m = v_m + \alpha d_j$  in which  $\alpha$  is computed by performing line search
  end
  Normalization:  $|v_m\rangle = \frac{|v_m\rangle}{\sqrt{\langle v_m | v_m \rangle}}$ 
end
The Gram-Schmidt procedure is performed to ensure that  $\{|v_m\rangle\}$  are orthogonal to each other.
end

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Algorithm 1: CG algorithm for finding smallest eigenpairs.

Results

The RPA correlation energy of following reaction is



We use equation (9) to directly solve the RPA correlation energy difference between two systems. The RPA correlation energy difference between two systems is solved with different eigenvalues which is showed in the Figure 1(a). When the RPA correlation energy is solved by using 600 eigenvalues, the RPA correlation difference starts to converge. Therefore, we used RPA correlation energy difference solving from 1200 eigenvalues to be the benchmark and compared with the RPA correlation energy difference solving from the KPM method. In Figure 1(b), we show the convergence of the RPA correlation energy difference with different number of random vectors for this two similar systems. The red solid line represents that two similar systems are sampled with the same random seed. The black dash line represents the RPA correlation energy difference solving using 1200 eigenvalues.

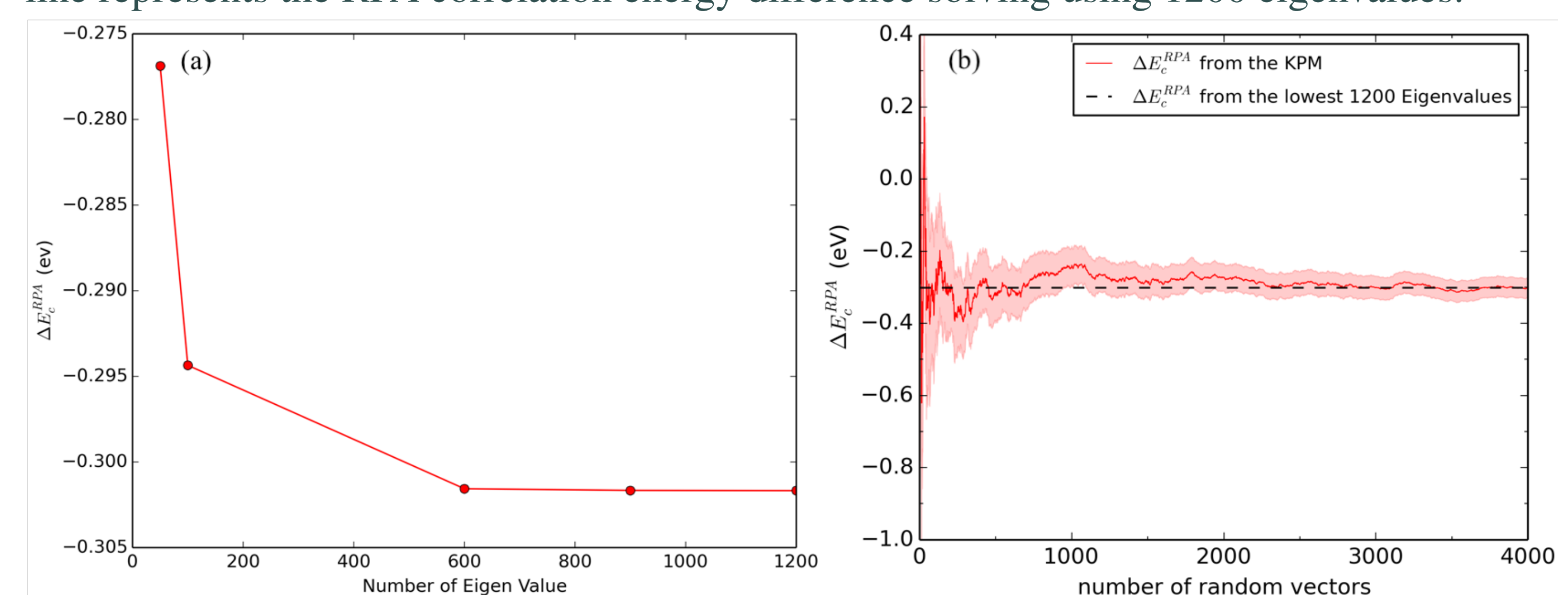


Figure 1: (a) The convergence of the RPA correlation energy difference (eV) between two systems with different number of eigenvalues. (b) The RPA correlation energy difference between two systems with different number of random vectors from the KPM and from directly solving 1200 eigenvalues.

Summary and Outlook

We are in the progress of implementing the atom-centered correlated sampling method in the ABINIT program, an open-source, plane-wave based on DFT program. In the future, this method will be used to obtain sufficiently accurate surface adsorption energies of molecules on solids to help us gain reliable understanding of heterogeneous catalysis with the atomic resolution.

Acknowledgments

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References

- [1] A. Weib , G. Willein, and A. Alvermann, and H. Fehske, Rev. Mod. Phys. **78**, 275 (2006)
- [2] N. L. Nguyen, N. Colonna, and S. de Gironcoli, Phys. Rev. B **90**, 045138 (2014)
- [3] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, Rev. of Mod. Phys. **64**, 4 (1992)
- [4] C. Huang, A. F. Voter, and D. Perez, Phys. Rev. B **87**, 214106 (2013)