

FHI-aims Cheat Sheet: RPA and the basis set extrapolation

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The random-phase approximation (RPA) is the state-of-the-art density-functional approximation (DFA) that address some notorious deficiencies of conventional DFAs in, for example, describing non-covalent interactions, reaction barrier heights, etc. Within the adiabatic-connection fluctuation-dissipation (ACFD) theorem, the RPA correlation energy E_c^{RPA} is expressed as:

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

Here $v = 1/|\mathbf{r} - \mathbf{r}'|$ is the bare Coulomb interaction kernel. $\chi_0(\mathbf{r}, \mathbf{r}'; iu)$ is Kohn-Sham (KS) independent-particle density response in imaginary frequency:

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = \sum_\sigma \sum_{n,m} \frac{(f_{n,\sigma} - f_{m,\sigma})}{iu + \epsilon_{n,\sigma} - \epsilon_{m,\sigma}} \phi_{n,\sigma}^*(\mathbf{r}) \phi_{m,\sigma}^*(\mathbf{r}') \phi_{n,\sigma}(\mathbf{r}) \phi_{m,\sigma}(\mathbf{r}'), \quad (2)$$

where $\phi_{n,\sigma}$ and $\epsilon_{n,\sigma}$ are the KS eigenfunctions and eigenenergies with Fermi occupation numbers $f_{n,\sigma}$.

Unfortunately, RPA suffers heavily from its well-known slow convergence with basis set convergence. In FHI-aims, we developed a series of numerically tabulated atom-centered orbital (NAO) basis sets with valence-correlation consistency (VCC), termed NAO-VCC-nZ (n = 2, 3, 4, 5). These basis sets are suitable for converging RPA total energies within the frozen-core algorithm. The basis set incompleteness error, including the basis set superposition error, can be gradually reduced with the increase of the index “n”, and can be removed using two-point extrapolation schemes:

$$E[\infty] = \frac{E[\mathbf{n}_1]n_1^3 - E[\mathbf{n}_2]n_2^3}{n_1^3 - n_2^3}. \quad (3)$$

Here $E[\mathbf{n}_1]$ is the RPA total energy calculated in conjunction with NAO-VCC-n₁Z.

How to begin?

1) Specified the keyword “total_energy_method” as “RPA” and “frozen_core_postSCF” as “1” to turn on the frozen-core RPA calculations in the `control.in`:

```
total_energy_method rpa
frozen_core_postSCF 1
```

2) Find the NAO-VCC-nZ basis sets from the FHI-aims repository. Then append them into the end of the control.in

What do we get?

1) After the calculation, you can find the RPA total energy at the end of the output file, shown as

```
DFT/HF total energy      :      -XXXXX.XXXXXXXXXX Ha,      -XXXXXX.XXXXXXXXXX eV
Exchange-only total energy :      -XXXXX.XXXXXXXXXX Ha,      -XXXXXX.XXXXXXXXXX eV
RPA total energy         :      -XXXXX.XXXXXXXXXX Ha,      -XXXXXX.XXXXXXXXXX eV
```

2) To approach the complete-basis-set (CBS) limit using Eq. 3, it is required at least two RPA calculations in conjunction with NAO-VCC-nZ basis sets with different indices “n”, for example n=4 and 5.

Attention!

These cheat sheets are not intended to substitute for reading the manuals of the programs involved and the original literature cited therein!

Have fun!