



In the exact PPLB theory, the ensemble energy should be linear with respect to the variation of the number of electron and the slope of the ensemble energy should be constant and equal to the ionization potential/electron affinity depending on which of left/right PPLB ensemble is used.

In practice the ensemble energy is not linear causing the error in the extraction of physical quantities like IP, EA,FG.

The idea is to build a weight-dependant exchange functional which correct the curvature-error in the total ensemble energy and to study if and how it improves the extracted IP,EA and FG.

The reference values are obtained from total difference energy for each functional, meaning not from an ensemble calculation.

Left PPLB ensemble : $E_0^\alpha = (1 - \alpha)E_0^N + \alpha E_0^{N-1}$

Ionization Potential : $\frac{dE_0^\alpha}{d\alpha} = E_0^{N-1} - E_0^N = \text{IP}^{\text{deriv}}$

Right PPLB ensemble : $E_0^\alpha = (1 - \alpha)E_0^N + \alpha E_0^{N+1}$

Electron affinity : $\frac{dE_0^\alpha}{d\alpha} = E_0^{N+1} - E_0^N = -\text{EA}^{\text{deriv}}$

Fundamental gap : $\text{FG} = \text{IP} - \text{EA} = \epsilon_{\text{KS}}^{\text{LUMO}} - \epsilon_{\text{KS}}^{\text{HOMO}} + \frac{dE_{\text{xc}}^\alpha}{d\alpha}$

	x	c	$-\epsilon_{\text{KS}}^{\text{HOMO}}$	IP^{deriv}	IP^{ref}	$-\epsilon_{\text{KS}}^{\text{LUMO}}$	EA^{deriv}	EA^{ref}	$\epsilon_{\text{KS}}^{\text{LUMO}} - \epsilon_{\text{KS}}^{\text{HOMO}}$	FG^{deriv}	FG^{ref}
left PPLB Li cc-pvdz $\delta N = -0.05$	HF		0.196405	0.196323	0.196311	-0.0123601	-0.0123549	-0.0156056	0.208765	0.208678	0.211917
	HF	VWN5	0.214634	0.214545	0.212652	0.0665225	-0.000441717	0.0221266	0.148112	0.214986	0.190525
	S51		0.109143	0.109097	0.184534	0.00647934	0.00647709	-0.0234851	0.102664	0.10262	0.208019
	CC1 for linear S51		0.108815	0.183499	0.184534	0.00647559	-0.0645201	-0.0234851	0.102339	0.248019	0.208019
	S51	VWN5	0.125648	0.125595	0.200892	0.0868882	0.0199066	0.0137471	0.0387594	0.105688	0.187144
	CC1 for linear S51-VWN5	VWN5	0.125315	0.199771	0.200892	0.0868654	-0.0508748	0.0137471	0.0384501	0.250646	0.187144
right PPLB Li cc-pvdz $\delta N = +0.05$	HF		0.186309	0.186252	0.196311	-0.0564574	-0.0219601	-0.0156056	0.242766	0.208213	0.211917
	HF	VWN5	0.205077	0.204991	0.212652	-0.0174711	-0.00841157	0.0221266	0.222548	0.213403	0.190525
	S51		0.0904967	0.090459	0.184534	-0.028362	0.0169085	-0.0234851	0.118859	0.0735505	0.208019
	CC2 for linear S51		0.0903296	0.128476	0.184534	-0.0283896	-0.0233326	-0.0234851	0.118719	0.151809	0.208019
	S51	VWN5	0.10755	0.107505	0.200892	0.0179713	0.0320812	0.0137471	0.0895785	0.0754235	0.187144
	CC2 for linear S51-VWN5	VWN5	0.107275	0.16646	0.200892	0.0179285	-0.0303418	0.0137471	0.0893464	0.196802	0.187144