What's New in Q-Chem

LB94 Asymptotically Corrected Exchange-Correlation (xc) Potential

Developers: Yu-Chuan Su, Jeng-Da Chai

Leeuwen and Baerends proposed a modeled exchange potential that has correct asymptotic behavior, which is not met by almost all GGA functionals and some hybrid functionals. We implemented the LB94 xc potential with an adiabatic LDA xc kernel, the so-called TDLDA/LB94 approach, which has been widely used for large systems. The LB94 xc potential shows correct asymptotic behavior, which is important for response properties in TDDFT calculations. Since LB94 xc potential is a gradient-corrected potential, it has much less computational costs than hybrid functionals. This function should be used for excitation energies, polarizabilities and hyperpolarizabilites in TDDFT calculations.

As can see in the table, the excitation energies of C2H4 molecule can be greatly improved by employing the LB94 xc potentials in the SCF step with a TDDFT calculation using an adiabatic LDA xc kernel. (6-311(2+,2+)G** basis is used in the calculations.)

State	BLYP	B3LYP	TDLDA /LB94	TDLDA /LBα	Expt.
V^3B_{1u}	4.31	4.06	4.44	4.49	4.36
V^1B_{1u}	7.09	7.35	7.70	8.02	8.00
R^3B_{3u}	6.10	6.51	6.74	7.05	6.98
R^1B_{3u}	6.16	6.58	7.22	7.38	7.11
R^3B_{1g}	6.58	7.03	7.61	7.87	7.79
R^1B_{1g}	6.60	7.08	7.53	7.28	7.80
R^1B_{2g}	6.55	7.10	7.77	7.66	7.90
R^3A_g	6.86	7.36	8.24	7.87	8.15
R^1A_g	6.92	7.35	8.42	8.03	8.28
MAE	1.02	0.66	0.15	0.18	-

Excitation energy of C_2H_4 (eV)

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LB94 Asymptotically Corrected Exchange-Correlation (xc) Potential (continued)

Publications:

R. van Leeuwen and E. J. Baerends, "Asymptotically correct exchange-correlation potential," Phys. Rev. A **49**, 2421 (1994)

P.R.T. Schipper, O.V. Gritsenko, S.J.A. van Gisbergen, E.J. Baerends, "Molecular calculations of excitation energies and (hyper)polarizabilities with a statistical average of orbital model exchange-correlation potentials," J. Chem. Phys. **112**, 1344, (2000)

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