Self-Consistent Field Solution for Anions: Effect of the Removal of Pseudo-Continuum States

Deepak Kumar and Ashish Kumar Gupta*

Department of Chemistry, Indian Institute of Technology Guwahati, Assam, India

E-mail: gupta@iitg.ac.in

Supporting Information

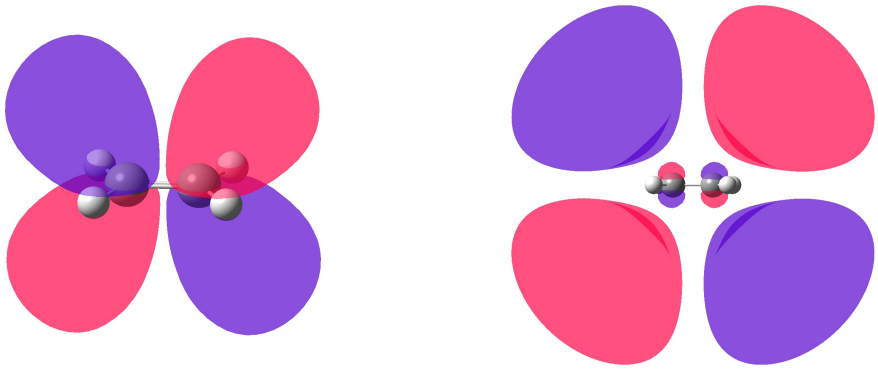
CAP box size used for C_2H_4 and HCHO in a.u.

Molecule	X	Y	Z
C_2H_4	7.10	4.65	3.40
HCHO	3.85	2.95	6.10

Ethylene anion ($C_2H_4^-$)

Cartesian coordinates in Angstroms for C_2H_4

Atom	X	Y	Z
C	0.6676247	0.0000000	0.0000000
C	-0.6676247	0.0000000	0.0000000
H	1.2300435	-0.9237114	0.0000000
H	1.2300435	0.9237114	0.0000000
H	-1.2300435	0.9237114	0.0000000
H	-1.2300435	-0.9237114	0.0000000



(a) Real/ isovalue=0.02 (b) Imaginary/ isovalue=0.003

Figure S1: Real and Imaginary part of SOMO for $C_2H_4^-$ using aug-cc-pVDZ+5p basis set at η_{opt} value after removal of psuedo-continuum states.

Formaldehyde anion ($HCHO^-$)

Cartesian coordinates in Angstroms for HCHO

Atom	X	Y	Z
O	0.0000000000	0.0000000000	-0.6716176471
C	0.0000000000	0.0000000000	0.5333823529
H	0.9429000000	0.0000000000	1.1209823529
H	-0.9429000000	0.0000000000	1.1209823529

(a) Real/ isovalue=0.02 (b) Imaginary/ isovalue=0.003

Figure S2: Real and Imaginary part of SOMO for $HCHO^-$ using aug-cc-pVDZ+5p basis set at η_{opt} value after removal of psuedo-continuum states.

Table S1: The real and imaginary part of the resonance energies for $C_2H_4^-$ at HF-level are tabulated for different box size using cc-pVDZ+5p basis set.

Box-size ($x_0/y_0/z_0$ in a.u.)	Real part (in eV)	Imaginary part (in eV)
6.0/6.0/6.0	1.98	0.58
6.5/6.5/6.5	1.99	0.52
7.0/7.0/7.0	2.00	0.46
7.5/7.5/7.5	2.00	0.44

Difference in computational time with all the states and with reduced states

Regarding the time taken for calculations: once the states are removed, the calculations will naturally become faster. For comparison, we have reported the calculation times for the neutral C_2H_4 molecule with all states included versus the times taken after the removal of pseudo-continuum states for the cc-pVTZ+7p/8p basis set. Data for CPU time taken with all the states and after removing pseudo-continuum states using cc-pVTZ+7p/8p basis sets for C_2H_4 is provided in Table S2.

Table S2: Tabular data for CPU time taken with all the states and after remoing pseudo-continuum states using cc-pVTZ+7p/8p basis sets for C_2H_4

Basis set	CPU time taken will all the states	CPU time taken with reduced number of states
cc-pVTZ+7p	1702 seconds	904 seconds
cc-pVTZ+8p	2007 seconds	983 seconds

Comparision of Energies at particular η for anionic and neutral species

At this particular η, MP2-level energies are also obtained for anionic and neutral species in both the cases(i.e., with all the states and with after the removal of pseudo-continuum states), which are provided in Table S3 and Table S4.

Table S3: Tabular data for HF and MP2 energies obtained with pseudo-continuum states and without pseudo-continuum states using cc-pVDZ+4p for C_2H_4.

Basis set/System	η-value	HF-energy with pseudo-continuum states	HF-energy without pseudo-continuum states	MP2-energy with pseudo-continuum states	MP2-energy without pseudo-continuum states
cc-pVDZ+4p/Anion	0.0280	(-77.93097,-0.01154)	(-77.93097,-0.01154)	(-78.23343,-0.014554)	(-78.23301,-0.01448)
cc-pVDZ+4p/Neutral	0.0280	(-78.04204,-0.00149)	(-78.04204,-0.00149)	(-78.33087,-0.00176)	(-78.33051,-0.00171)

Table S4: Tabular data for HF and MP2 energies obtained with pseudo-continuum states and without pseudo-continuum states using cc-pVDZ+5p for HCHO.

Basis set/System	η-value	HF-energy with pseudo-continuum states	HF-energy without pseudo-continuum states	MP2-energy with pseudo-continuum states	MP2-energy without pseudo-continuum states
cc-pVDZ+5p/Anion	0.0100	(-113.81900,-0.00422)	(-113.81900,-0.00422)	(-114.16258,-0.00719)	(-114.16203,-0.00723)
cc-pVDZ+5p/Neutral	0.0100	(-113.88349,-0.00024)	(-113.88349,-0.00024)	(-114.21867,-0.00035)	(-114.21824,-0.00038)

The results for MP2-level calculations are obtained using cc-pVDZ+4p basis set for C_2H_4 and using cc-pVDZ+5p basis set for HCHO at higher η ($\eta > \eta_{opt}$). For C_2H_4, the difference of real part of energy at MP2 level for anionic system is 0.00042 a.u. (0.011eV) and for neutral system is 0.00036 a.u. (0.0098 eV) as shown in Table S5. For HCHO, the difference of real part of energy at MP2 level for anionic system is 0.00055 a.u. (0.015 eV) and for neutral system is 0.00043 a.u. (0.012 eV) as also shown in Table S5. Similarly, the difference in the imaginary part is also less than 0.01 eV.

Table S5: Difference of total energies of anionic and neutral species for C_2H_4 and HCHO at higher η ($\eta > \eta_{opt}$.

Molecule	Difference in MP2 energy for neutral system (in eV)	Difference in MP2 energy for anionic system (in eV)
C_2H_4	(0.0098,0.0014)	(0.0114,0.0021)
HCHO	(0.012,0.0008)	(0.015,0.0011)

These comparisons have shown that the effect is in the range of 0.01 eV or less, which can be considered negligible. The reason for this negligible change in the correlation energy could be due to no significant mixing of states at higher η as these pseudo-continuum states have been rotated away from the SOMO (or localised state) in complex plane. Furthermore, the resonance energy, defined as the difference between the total energy of the anion and the total energy of the neutral atom, remains unaffected by the removal of the pseudo-continuum states.Hence, it is anticipated that if an anionic SCF solution were to exist at other η values, the effect of removal of pseudo-continuum states on the correlation energy would be similar to that seen in neutral molecules. Therefore, one would expect the errors to cancel out, as demonstrated in calculations involving anionic SCF with continuum states and without pseudo-continuum states.

Polarizabilities for both the molecules

Polarizabilities are calculated for both molecules at the CISD and MP2 levels, considering all states as well as a reduced number of states, using Gaussian software. For this purpose, we performed CISD and MP2 calculations with the cc-pVDZ+5p basis set, applying an external electric field of 0.001 a.u. along the principal axis for C_2H_4 and HCHO. It is found that the change in polarizability for the CISD method is minor, while a drastic change in polarizability is observed with the MP2 method, as shown in Table S6 and Table S7. Additionally, we performed calculations for the energies of both neutral C_2H_4 and HCHO molecules to assess the effect of removing pseudo-continuum states at the CISD level. The results indicate that the energy change is approximately 1 percent for C_2H_4 and around 3 percent for HCHO, as detailed in Table S8.

Table S6: Tabular data for polarizibilty obtained at MP2 and CISD level using cc-pVDZ+5p for both the cases(i.e., with all the states and with reduced number of states) of neutral C_2H_4 molecule.

Basis Set	Level of Theory	With all states	with reduced number of states
cc-pVDZ+5p	CISD	33.4234	33.7229
cc-pVDZ+5p	MP2	33.0414	-153.850

Table S7: Tabular data for polarizibilty obtained at MP2 and CISD level using cc-pVDZ+5p for both the cases(i.e., with all the states and with reduced number of states) of neutral HCHO molecule.

Basis Set	Level of Theory	With all states	with reduced number of states
cc-pVDZ+5p	CISD	14.1217	15.3316
cc-pVDZ+5p	MP2	14.7083	3.5995

Table S8: The table presents the correlation energy at CISD level obtained with all the states and with removed number of states pseudo-continuum states. It also includes the differences and percentage differences, along with the number of states removed using various basis sets for both neutral C_2H_4 and HCHO molecules.

System/Basis Set	Correlation Energy with pseudo-continuum states(in a.u.)	Correlation Energy without pseudo-continuum states(in a.u.)	Difference in Correlation Energy (in a.u.)	% Difference	Number of states removed
C_2H_4/cc-pVDZ+5p	-0.2845	-0.2815	0.0030	1.05	18
HCHO/cc-pVDZ+5p	-0.3158	-0.3057	0.0101	3.19	15