STOs vs. GTOs

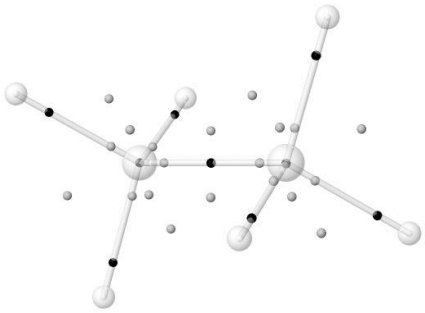
The current work utilizes Slater-type functions STOs as basis for molecular orbitals, while the majority of quantum chemical programs exploit Gaussian-type functions GTOs. The difference is explored in $\nu(\mathbf{r})$ calculations of C_2H_6.
To achieve consistency, the geometry of ethane has been optimized under C_{3v}-symmetry constraint using PBE/TZVP(STO) and PBE/TZVP(GTO) calculations. The optimized geometries are virtually identical; a comparison is given in the table below.

	GTO			STO			
	x	y	z	x	y	z	ΔR
C	0.000000	0.000000	-0.764695	0.000000	0.000000	-0.764738	4.300E-05
C	0.000000	0.000000	0.764932	0.000000	0.000000	0.764896	3.600E-05
H	0.000000	1.024264	1.166814	0.000000	1.024226	1.166463	3.531E-04
H	-0.887039	-0.512132	1.166814	-0.887006	-0.512113	1.166463	3.531E-04
H	0.887039	-0.512132	1.166814	0.887006	-0.512113	1.166463	3.531E-04
H	0.000000	-1.024143	-1.167287	0.000000	-1.024163	-1.166620	6.673E-04
H	0.886934	0.512071	-1.167287	0.886952	0.512082	-1.166620	6.673E-04
H	-0.886934	0.512071	-1.167287	-0.886952	0.512082	-1.166620	6.673E-04

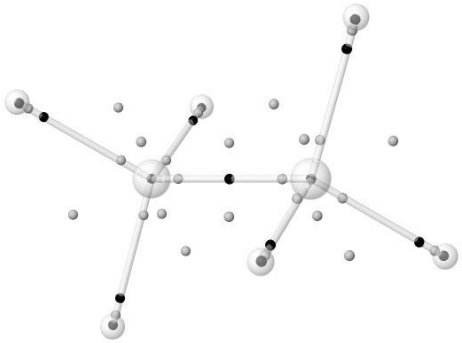
Both calculations produce consistent $\nu(\mathbf{r})$ topologies with PoHo# = 1. The details are given in the table below:

	(3,-3)	(3,-1)	(3,1)	(3,3)
PBE/TZVP(STO)	9	20	20	8
PBE/TZVP(GTO)	15	26	20	8

Since an STO has a cusp at its origin, while a GTO smoothly proceeds to zero slope, and since the basis functions are centered at atomic positions, the innermost core region is inadequately described by GTOs. The GTO calculations result in six additional (3,-3) CPs, and six additional (3,-1) CPs. These additional CPs are located in close vicinity to the hydrogen atoms, as show in the pictures below:



PBE/TZVP(STO)



PBE/TZVP(GTO)

A detailed comparison of (3,-3) and (3,-1) CPs is given in the table below:

	GTO				STO				ΔR	Δν (GTO-STO)
	x	y	z	ν	x	y	z	ν		
Xa	0.00000	0.00000	-0.76469	0.99896	0.00017	0.00010	-0.76415	0.79673	5.75E-04	2.02E-01
Xa	0.00000	0.00000	0.76493	0.99896	-0.00031	0.00018	0.76471	0.79722	4.21E-04	2.02E-01
Xa	0.00000	1.01188	1.16185	0.98990						
Xa	0.00000	-1.01176	-1.16232	0.98990						
Xa	-0.87631	-0.50594	1.16185	0.98990						
Xa	0.87631	-0.50594	1.16185	0.98990						
Xa	0.87621	0.50588	-1.16232	0.98990						
Xa	-0.87621	0.50588	-1.16232	0.98990						
Xa	0.71516	-0.41290	1.08672	0.91719	0.65603	-0.37876	1.05854	0.91279	7.39E-02	4.40E-03
Xa	-0.71516	-0.41290	1.08672	0.91719	-0.65603	-0.37876	1.05854	0.91279	7.39E-02	4.40E-03
Xa	0.00000	0.82579	1.08672	0.91719	0.00000	0.75752	1.05854	0.91279	7.39E-02	4.40E-03
Xa	0.71507	0.41285	-1.08701	0.91716	0.65600	0.37874	-1.05859	0.91278	7.39E-02	4.38E-03
Xa	-0.71507	0.41285	-1.08701	0.91716	-0.65600	0.37874	-1.05859	0.91278	7.39E-02	4.38E-03
Xa	0.00000	-0.82569	-1.08700	0.91716	0.00000	-0.75748	-1.05859	0.91278	7.39E-02	4.38E-03
Xa	0.00000	0.00000	0.00008	0.82161	0.00000	0.00000	0.00006	0.81919	2.00E-05	2.42E-03
Xb	-0.81622	-0.47124	1.13400	0.86300						
Xb	0.81622	-0.47124	1.13400	0.86300						
Xb	0.00000	0.94249	1.13400	0.86300						
Xb	0.81613	0.47120	-1.13440	0.86295						
Xb	-0.81613	0.47120	-1.13440	0.86295						
Xb	0.00000	-0.94239	-1.13440	0.86295						
Xb	0.00000	0.49102	-1.10795	0.50726	0.00000	0.49129	-1.10753	0.50747	4.99E-04	-2.10E-04
Xb	0.42524	-0.24551	-1.10793	0.50726	0.42547	-0.24565	-1.10753	0.50747	4.82E-04	-2.10E-04
Xb	-0.42524	-0.24551	-1.10793	0.50726	-0.42547	-0.24565	-1.10753	0.50747	4.82E-04	-2.10E-04
Xb	0.00000	-0.49104	1.10806	0.50722	0.00000	-0.49131	1.10763	0.50745	5.08E-04	-2.30E-04
Xb	-0.42526	0.24553	1.10804	0.50722	-0.42549	0.24566	1.10763	0.50745	4.88E-04	-2.30E-04
Xb	0.42526	0.24553	1.10804	0.50722	0.42549	0.24566	1.10763	0.50745	4.88E-04	-2.30E-04
Xb	-0.42332	-0.24440	0.42271	0.49960	-0.42376	-0.24466	0.42346	0.50077	9.08E-04	-1.17E-03
Xb	0.42332	-0.24440	0.42271	0.49960	0.42376	-0.24466	0.42346	0.50077	9.08E-04	-1.17E-03
Xb	0.00000	0.48880	0.42271	0.49959	0.00000	0.48932	0.42346	0.50077	9.13E-04	-1.18E-03
Xb	0.42339	0.24444	-0.42265	0.49957	0.42379	0.24468	-0.42338	0.50075	8.66E-04	-1.18E-03
Xb	-0.42339	0.24444	-0.42265	0.49957	-0.42379	0.24468	-0.42338	0.50075	8.66E-04	-1.18E-03
Xb	0.00000	-0.48888	-0.42265	0.49956	0.00000	-0.48935	-0.42338	0.50075	8.68E-04	-1.19E-03
Xb	-0.21704	-0.12531	0.84543	0.16528	-0.21657	-0.12504	0.84766	0.17040	2.29E-03	-5.12E-03
Xb	0.21704	-0.12531	0.84543	0.16528	0.21657	-0.12504	0.84766	0.17040	2.29E-03	-5.12E-03
Xb	0.00000	0.25062	0.84542	0.16528	0.00000	0.25007	0.84766	0.17040	2.31E-03	-5.12E-03
Xb	0.21703	0.12530	-0.84526	0.16527	0.21656	0.12503	-0.84753	0.17039	2.33E-03	-5.12E-03
Xb	-0.21703	0.12530	-0.84526	0.16527	-0.21656	0.12503	-0.84753	0.17039	2.33E-03	-5.12E-03
Xb	0.00000	-0.25060	-0.84525	0.16527	0.00000	-0.25006	-0.84753	0.17039	2.34E-03	-5.12E-03
Xb	0.00000	0.00000	-0.49865	0.16082	0.00000	0.00000	-0.49839	0.16542	2.60E-04	-4.60E-03
Xb	0.00000	0.00000	0.49888	0.16081	0.00000	0.00000	0.49855	0.16542	3.30E-04	-4.61E-03

Notable differences are found for two ot the(3,-3) CPs, which are located at approximately the same position close to the carbon atoms, but which show differences in $\nu(\mathbf{r})$. The fact that a GTO approaches zero slope at the position of a nucleus is reflected in the $\nu(\mathbf{r})$ values (0.99896) approaching 1.0. Slight differences in the corresponding STO $\nu(\mathbf{r})$ values are due to the fact that the (3,-3) CPs are estimated as approximate endpoints of MaxKCLs.

A detailed comparison of (3,1) and (3,3) CPs is given in the table below:

	GTO				STO				ΔR	Δν (GTO-STO)
	x	y	z	ν	x	y	z	ν		
Xc	0.46693	-0.26960	-0.56894	0.41881	0.47107	-0.27197	-0.57043	0.41832	5.00E-03	4.90E-04
Xc	-0.46693	-0.26960	-0.56894	0.41881	-0.47107	-0.27197	-0.57043	0.41832	5.00E-03	4.90E-04
Xc	0.00000	0.53918	-0.56895	0.41881	0.00000	0.54394	-0.57043	0.41832	4.98E-03	4.90E-04
Xc	-0.46690	0.26958	0.56908	0.41879	-0.47105	0.27196	0.57054	0.41831	5.00E-03	4.80E-04
Xc	0.46690	0.26958	0.56908	0.41879	0.47105	0.27196	0.57054	0.41831	5.00E-03	4.80E-04
Xc	0.00000	-0.53913	0.56909	0.41878	0.00000	-0.54392	0.57054	0.41831	5.00E-03	4.70E-04
Xc	0.00000	-0.00001	-1.33996	0.41204	0.00000	0.00000	-1.34324	0.41043	3.28E-03	1.61E-03
Xc	0.00000	0.00001	1.34018	0.41203	0.00000	0.00000	1.34338	0.41043	3.20E-03	1.60E-03
Xc	0.00000	-0.23434	0.89894	0.15745	0.00000	-0.23182	0.90555	0.16033	7.07E-03	-2.88E-03
Xc	-0.20295	0.11717	0.89893	0.15745	-0.20076	0.11591	0.90555	0.16033	7.09E-03	-2.88E-03
Xc	0.20295	0.11717	0.89893	0.15745	0.20076	0.11591	0.90555	0.16033	7.09E-03	-2.88E-03
Xc	0.00000	0.23431	-0.89876	0.15744	0.00000	0.23181	-0.90541	0.16032	7.10E-03	-2.88E-03
Xc	0.20292	-0.11716	-0.89875	0.15744	0.20075	-0.11590	-0.90541	0.16032	7.12E-03	-2.88E-03
Xc	-0.20292	-0.11716	-0.89875	0.15744	-0.20075	-0.11590	-0.90541	0.16032	7.12E-03	-2.88E-03
Xc	0.00000	0.20259	0.58510	0.15626	0.00000	0.20730	0.58835	0.15885	5.72E-03	-2.59E-03
Xc	-0.17545	-0.10129	0.58511	0.15626	-0.17953	-0.10365	0.58835	0.15885	5.72E-03	-2.59E-03
Xc	0.17545	-0.10129	0.58511	0.15626	0.17953	-0.10365	0.58835	0.15885	5.72E-03	-2.59E-03
Xc	0.00000	-0.20271	-0.58501	0.15626	0.00000	-0.20735	-0.58825	0.15885	5.66E-03	-2.59E-03
Xc	0.17556	0.10135	-0.58502	0.15626	0.17957	0.10367	-0.58825	0.15885	5.65E-03	-2.59E-03
Xc	-0.17556	0.10135	-0.58502	0.15626	-0.17957	0.10367	-0.58825	0.15885	5.65E-03	-2.59E-03
Xd	-0.21618	0.12481	0.64936	0.15191	-0.22024	0.12716	0.65344	0.15232	6.22E-03	-4.10E-04
Xd	0.21618	0.12481	0.64936	0.15191	0.22024	0.12716	0.65344	0.15232	6.22E-03	-4.10E-04
Xd	0.00000	-0.24962	0.64937	0.15190	0.00000	-0.25431	0.65344	0.15232	6.21E-03	-4.20E-04
Xd	0.21623	-0.12484	-0.64925	0.15190	0.22026	-0.12717	-0.65332	0.15232	6.18E-03	-4.20E-04
Xd	-0.21623	-0.12484	-0.64925	0.15190	-0.22026	-0.12717	-0.65332	0.15232	6.18E-03	-4.20E-04
Xd	0.00000	0.24968	-0.64925	0.15190	0.00000	0.25433	-0.65332	0.15232	6.18E-03	-4.20E-04
Xd	0.00000	0.00001	1.04091	0.14943	0.00000	0.00000	1.04324	0.14989	2.33E-03	-4.60E-04
Xd	0.00000	-0.00001	-1.04068	0.14943	0.00000	0.00000	-1.04308	0.14989	2.40E-03	-4.60E-04

The results of PBE/TZVP(STO) and PBE/TZVP(GTO)calculations are virtually identical.