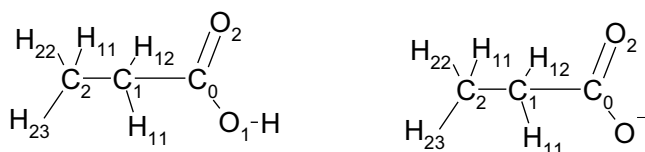


## Appendix

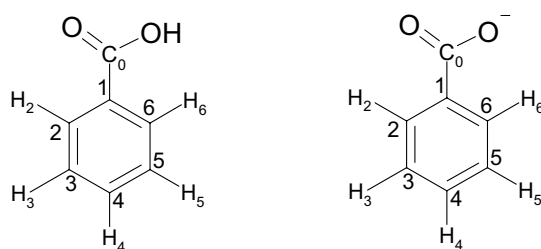
### Appendix A

**Table A.1a:** Atomic partial charges for propionic acid in both protonation states were derived from different QC ESP (Hartree-Fock (HF), Becke<sup>1/2</sup>) and B3LYP) using the RESP procedure as described in Chapter 2.7. For each of the three QC methods I applied the 6-31G\*\* and 6-31++G\*\* basis set.



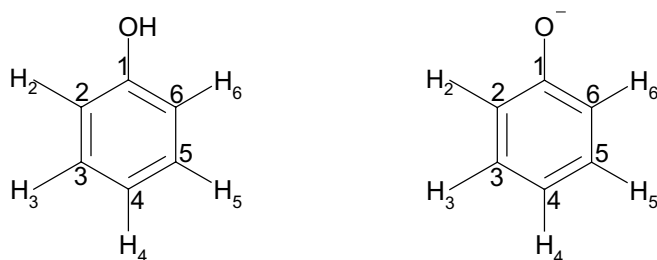
basis	propionic acid			propionic acid (anion)		
	6-31G**			6-31G**		
method	HF	Becke <sup>1/2</sup>	B3LYP	HF	Becke <sup>1/2</sup>	B3LYP
H	0.4502	0.4301	0.4114			
O <sub>1</sub>	-0.6413	-0.5846	-0.5514	-0.8411	-0.7780	-0.7459
O <sub>2</sub>	-0.6251	-0.5618	-0.5321	-0.8071	-0.7455	-0.7162
C <sub>0</sub>	0.7445	0.6476	0.6059	0.8055	0.6969	0.6484
C <sub>1</sub>	0.0042	-0.0102	-0.0108	0.0170	-0.0317	-0.0349
H <sub>11</sub>	0.0319	0.0402	0.0383	-0.0348	0.0175	0.0190
H <sub>12</sub>	0.0372	0.0456	0.0435	-0.0299	0.0377	-0.0445
C <sub>2</sub>	-0.1592	-0.1883	-0.1670	-0.1327	-0.1505	-0.1207
H <sub>21</sub>	0.0538	0.0620	0.0556	0.0209	0.0242	0.0145
H <sub>22</sub>	0.0551	0.0631	0.0567	0.0263	0.0287	0.0182
H <sub>23</sub>	0.0488	0.0563	0.0499	-0.0241	0.0239	-0.0349
basis	6-31++G**			6-31++G**		
method	HF	Becke <sup>1/2</sup>	B3LYP	HF	Becke <sup>1/2</sup>	B3LYP
H	0.4552	0.4402	0.4232			
O	-0.6588	-0.6198	-0.5928	-0.9026	-0.8665	-0.8462
O	-0.6501	-0.6036	-0.5820	-0.8633	-0.8277	-0.8099
C <sub>0</sub>	0.7773	0.7107	0.6815	0.9075	0.8458	0.8165
C <sub>1</sub>	0.0152	0.0014	-0.0002	0.0676	0.1054	0.1218
H <sub>11</sub>	0.0271	0.0328	0.0309	-0.0535	-0.0712	-0.0827
H <sub>12</sub>	0.0313	0.0371	0.0353	-0.0508	-0.0676	-0.0785
C <sub>2</sub>	-0.1273	-0.1340	-0.1082	-0.0614	-0.0437	-0.0117
H <sub>21</sub>	0.0441	0.0452	0.0376	-0.0021	-0.0120	-0.0232
H <sub>22</sub>	0.0455	0.0467	0.0391	0.0046	0.0052	-0.0165
H <sub>23</sub>	0.0407	0.0432	0.0357	-0.0459	-0.0574	-0.0697

**Table A.1b:** Atomic partial charges for benzoic acid in both protonation states were derived from different QC ESP (Hartree-Fock (HF), Becke<sup>1/2</sup>) and B3LYP) using the RESP procedure as described in Chapter 2.7. For each of the three QC methods I applied the 6-31G\*\* and 6-31++G\*\* basis set.



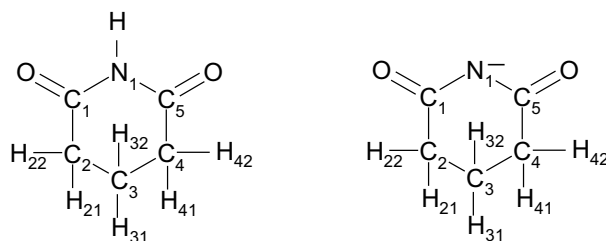
basis method	benzoic acid			benzoic acid (anion)		
	HF	6-31G** Becke <sup>1/2</sup>	B3LYP	HF	6-31G** Becke <sup>1/2</sup>	B3LYP
H	0.4450	0.4270	0.4073			
O	-0.6255	-0.5728	-0.5398	-0.7794	-0.7182	-0.6849
O	-0.5908	-0.5298	-0.5096	-0.7796	-0.7183	-0.6846
C <sub>0</sub>	0.7102	0.6137	0.5777	0.7543	0.6559	0.6148
C <sub>1</sub>	0.0024	0.0147	0.0130	0.0132	0.0097	0.0040
C <sub>2</sub>	-0.1513	-0.1370	-0.1151	-0.1476	-0.1287	-0.1087
H <sub>2</sub>	0.1544	0.1373	0.1207	0.1227	0.1018	0.0832
C <sub>3</sub>	-0.1221	-0.1087	-0.0976	-0.1487	-0.1419	-0.1371
H <sub>3</sub>	0.1309	0.1215	0.1090	0.0957	0.0845	0.0732
C <sub>4</sub>	-0.0971	-0.0986	-0.0868	0.1521	-0.1479	-0.1471
H <sub>4</sub>	0.1307	0.1208	0.1074	0.1002	0.0881	0.0770
C <sub>5</sub>	-0.1397	-0.1183	-0.1027	-0.1485	-0.1417	-0.1367
H <sub>5</sub>	0.1333	0.1221	0.1087	0.0959	0.0847	0.0734
C <sub>6</sub>	-0.1348	-0.1319	-0.1157	-0.1483	-0.1294	-0.1097
H <sub>6</sub>	0.1543	0.1340	0.1235	0.1222	0.1015	0.0830
basis method	6-31++G**			6-31++G**		
	HF	Becke <sup>1/2</sup>	B3LYP	HF	Becke <sup>1/2</sup>	B3LYP
H	0.4513	0.4368	0.4195			
O	-0.6428	-0.6051	-0.5805	-0.8254	-0.7865	-0.7683
O	-0.6048	-0.5567	-0.5390	-0.8256	-0.7864	-0.7684
C <sub>0</sub>	0.7245	0.6527	0.6275	0.8272	0.7658	0.7437
C <sub>1</sub>	0.0223	0.0369	0.0302	0.0578	0.0641	0.0564
C <sub>2</sub>	-0.1564	-0.1474	-0.1266	-0.1690	-0.1590	-0.1415
H <sub>2</sub>	0.1615	0.1455	0.1298	0.1379	0.1209	0.1045
C <sub>3</sub>	-0.1346	-0.1156	-0.1040	-0.1542	-0.1411	-0.1309
H <sub>3</sub>	0.1351	0.1257	0.1140	0.0997	0.0864	0.0726
C <sub>4</sub>	-0.0944	-0.1018	-0.0913	-0.1674	-0.1625	-0.1498
H <sub>4</sub>	0.1342	0.1247	0.1123	0.1057	0.0921	0.0780
C <sub>5</sub>	-0.1492	-0.1209	-0.1055	-0.1541	-0.1412	-0.1309
H <sub>5</sub>	0.1342	0.1257	0.1133	0.1000	0.0868	0.0730
C <sub>6</sub>	-0.1458	-0.1499	-0.1341	-0.1697	-0.1594	-0.1419
H <sub>6</sub>	0.16215	0.1496	0.1346	0.1371	0.1200	0.1036

**Table A.1c:** Atomic partial charges for phenol in both protonation states were derived from different QC ESP (Hartree-Fock (HF), Becke( $1/2$ ) and B3LYP) using the RESP procedure as described in Chapter 2.7. For each of the three QC methods I applied the 6-31G\*\* and 6-31++G\*\* basis set.



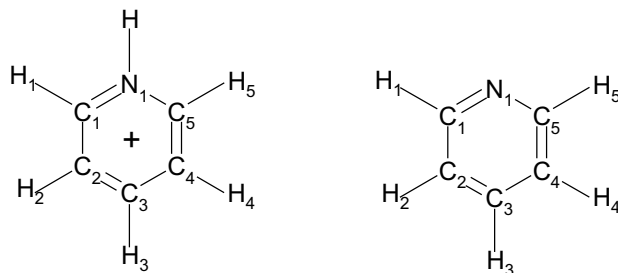
basis	phenol			phenoxyl		
	HF	6-31G** Becke $^{1/2}$	B3LYP	HF	6-31G** Becke $^{1/2}$	B3LYP
H	0.4219	0.4059	0.3949	-0.8215	-0.7492	-0.7162
O	-0.6211	-0.5709	-0.5419	0.7206	0.6074	0.5503
C <sub>1</sub>	0.4757	0.4073	0.3704	-0.4851	-0.4129	-0.3682
C <sub>2</sub>	-0.3930	-0.3374	-0.3062	0.1193	0.0990	0.0811
H <sub>2</sub>	0.1698	0.1494	0.1349	-0.0134	-0.0558	-0.0690
C <sub>3</sub>	-0.0342	-0.0490	-0.0542	0.0802	0.0684	0.0558
H <sub>3</sub>	0.1272	0.1168	0.1091	-0.4071	-0.3465	-0.3099
C <sub>4</sub>	-0.2178	-0.1844	-0.1635	0.1069	0.0914	0.0766
H <sub>4</sub>	0.1366	0.1223	0.1122	-0.0105	-0.0529	-0.0661
C <sub>5</sub>	-0.0805	-0.0914	-0.0929	0.0794	0.0676	0.0550
H <sub>5</sub>	0.1323	0.1215	0.1131	-0.4889	-0.4163	-0.3715
C <sub>6</sub>	-0.2985	-0.2521	-0.2247	0.1200	0.0998	0.0819
H <sub>6</sub>	0.1815	0.1620	0.1488			
basis	6-31++G**			6-31++G**		
method	HF	Becke $^{1/2}$	B3LYP	HF	Becke $^{1/2}$	B3LYP
H	0.4314	0.4221	0.4080	-0.8947	-0.8516	-0.8278
O	-0.6532	-0.6216	-0.5962	0.8470	0.7735	0.7176
C <sub>1</sub>	0.5221	0.4714	0.4384	-0.5309	-0.4658	-0.4176
C <sub>2</sub>	-0.4227	-0.3755	-0.3382	0.1287	0.1079	0.0900
H <sub>2</sub>	0.4314	0.1629	0.1464	0.0121	-0.0259	-0.0423
C <sub>3</sub>	-0.0277	-0.0462	-0.0512	0.0840	0.0723	0.0597
H <sub>3</sub>	0.1788	0.1233	0.1127	-0.4543	-0.3988	-0.3545
C <sub>4</sub>	-0.2336	-0.1994	-0.1722	0.1148	0.1004	0.0854
H <sub>4</sub>	0.1366	0.1299	0.1163	0.0178	-0.0194	-0.0359
C <sub>5</sub>	-0.0763	-0.0926	-0.0944	0.0824	0.0704	0.0578
H <sub>5</sub>	0.1904	0.1282	0.1173	-0.5370	-0.4723	-0.4238
C <sub>6</sub>	-0.3193	-0.2776	-0.2460	0.1300	0.1093	0.0913
H <sub>6</sub>	0.1314	0.1751	0.1590			

**Table A.1d:** Atomic partial charges for glutarimide in both protonation states were derived from different QC ESP (Hartree-Fock (HF), Becke( $1/2$ ) and B3LYP) using the RESP procedure as described in Chapter 2.7. For each of the three QC methods I applied the 6-31G\*\* and 6-31++G\*\* basis set.



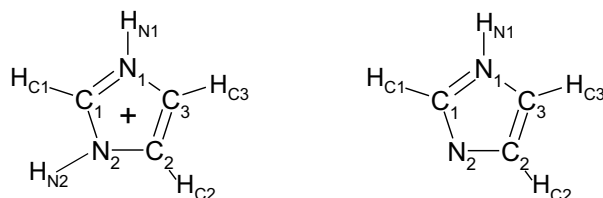
basis method	glutarimide			glutarimide anion		
	HF	Becke $^{1/2}$	B3LYP	HF	Becke $^{1/2}$	B3LYP
H	0.3709	0.3541	0.3348	-0.9611	-0.8848	-0.8392
N	-0.6562	-0.5933	-0.5460	0.8900	0.8035	0.7536
C <sub>1</sub>	0.7127	0.6364	0.5950	-0.7521	-0.6892	-0.6600
O <sub>1</sub>	-0.5823	-0.5212	-0.4937	-0.3163	-0.3162	-0.2889
C <sub>2</sub>	-0.2296	-0.2484	-0.2303	0.0543	0.0547	0.0442
H <sub>21</sub>	0.0894	0.0964	0.0895	0.0378	0.0349	0.0232
H <sub>22</sub>	0.0798	0.0853	0.0786	0.2162	-0.3104	-0.2818
C <sub>3</sub>	0.1150	0.1029	0.1001	-0.0358	-0.0548	-0.0356
H <sub>31</sub>	0.0143	0.0197	0.0167	-0.0563	-0.0559	-0.0614
H <sub>32</sub>	0.0162	0.0194	0.0161	-0.3129	0.1955	0.1906
C <sub>4</sub>	-0.2301	-0.2481	-0.2295	0.0554	0.0548	0.0439
H <sub>41</sub>	0.0898	0.0965	0.0894	0.0343	0.0305	0.0185
H <sub>42</sub>	0.0795	0.0848	0.0779	0.8944	0.7996	0.7500
C <sub>5</sub>	0.7116	0.6356	0.5942	-0.7479	-0.6856	-0.6570
O <sub>5</sub>	-0.5810	-0.5201	-0.4928	-0.9611	-0.8848	-0.8392
basis method	6-31++G**			6-31++G**		
	HF	Becke $^{1/2}$	B3LYP	HF	Becke $^{1/2}$	B3LYP
H	0.3750	0.3627	0.3446	-1.0041	-0.9678	-0.9349
N	-0.6628	-0.6236	-0.5858	0.9534	0.9088	0.8784
C <sub>1</sub>	0.7334	0.6872	0.6589	-0.8000	-0.7607	-0.7427
O <sub>1</sub>	-0.6095	-0.5661	-0.5449	-0.2931	-0.2889	-0.2676
C <sub>2</sub>	0.1347	-0.2406	-0.2294	0.0396	0.0312	0.0215
H <sub>21</sub>	0.0832	0.0880	0.0814	0.0286	0.0189	0.0076
H <sub>22</sub>	0.0772	0.0818	0.0752	0.2846	0.3144	-0.2584
C <sub>3</sub>	-0.2163	0.1517	0.1614	-0.0645	-0.0798	-0.0878
H <sub>31</sub>	0.0057	0.0008	-0.0059	-0.0744	-0.0876	-0.0961
H <sub>32</sub>	0.0116	0.0089	0.0030	-0.2883	-0.2811	0.3223
C <sub>4</sub>	-0.2167	-0.2412	-0.2282	0.04010	0.0304	0.0199
H <sub>41</sub>	0.0835	0.0880	0.0812	0.0251	0.0144	0.0028
H <sub>42</sub>	0.0769	0.0812	0.0744	0.94902	0.9052	0.8752
C <sub>5</sub>	0.7324	0.6863	0.6580	-0.7960	-0.7575	-0.7401
O <sub>5</sub>	-0.6082	-0.5650	-0.5439			

**Table A.1e:** Atomic partial charges for pyridine in both protonation states were derived from different QC ESP (Hartree-Fock (HF), Becke<sup>1/2</sup>) and B3LYP) using the RESP procedure as described in Chapter 2.7. For each of the three QC methods I applied the 6-31G\*\* and 6-31++G\*\* basis set.



basis	pyridine cation			pyridine		
	6-31G**			6-31G**		
method	HF	Becke <sup>1/2</sup>	B3LYP	HF	Becke <sup>1/2</sup>	B3LYP
H	0.3572	0.3453	0.3322			
N	-0.2004	-0.1227	-0.0963	-0.6911	-0.6483	-0.6253
C <sub>1</sub>	0.0935	0.0443	0.0342	0.4997	0.4707	0.4557
H <sub>1</sub>	0.1881	0.1824	0.1729	0.0201	0.0120	0.0043
C <sub>2</sub>	-0.1885	-0.1186	-0.0878	-0.5274	-0.4833	-0.4468
H <sub>2</sub>	0.1914	0.1793	0.1676	0.1848	0.1717	0.1560
C <sub>3</sub>	0.1082	0.0446	0.0372	0.2548	0.2311	0.2215
H <sub>3</sub>	0.1647	0.1616	0.1524	0.0816	0.0746	0.0650
C <sub>4</sub>	-0.1898	-0.1193	-0.0884	-0.5279	-0.4838	-0.4473
H <sub>4</sub>	0.1911	0.1790	0.1673	0.1849	0.1718	0.1561
C <sub>5</sub>	0.0968	0.0420	0.0361	0.5009	0.4718	0.4568
H <sub>5</sub>	0.1876	0.1821	0.1727	0.0197	0.0117	0.0040
basis	6-31++G**			6-31++G**		
method	HF	Becke <sup>1/2</sup>	B3LYP	HF	Becke <sup>1/2</sup>	B3LYP
H	0.3552	0.3436	0.3436			
N	-0.1957	-0.1259	-0.1259	-0.7320	-0.7053	-0.6891
C <sub>1</sub>	0.0975	0.0454	0.0454	0.5409	0.5247	0.5135
H <sub>1</sub>	0.1858	0.1822	0.1822	0.0155	0.0042	-0.0038
C <sub>2</sub>	-0.1949	-0.1238	-0.1238	-0.5643	-0.5236	-0.4876
H <sub>2</sub>	0.1919	0.1804	0.1804	0.1927	0.1806	0.1655
C <sub>3</sub>	0.1150	0.0512	0.0512	0.2809	0.2596	0.2489
H <sub>3</sub>	0.1634	0.1617	0.1617	0.0813	0.0736	0.0645
C <sub>4</sub>	-0.1962	-0.1246	-0.1246	-0.5651	-0.5242	-0.4882
H <sub>4</sub>	0.1916	0.1800	0.1800	0.1928	0.1807	0.1656
C <sub>5</sub>	0.1011	0.0481	0.0481	0.5424	0.5261	0.5148
H <sub>5</sub>	0.1853	0.1818	0.1818	0.0150	0.0038	-0.0041

**Table A.1f:** Atomic partial charges for imidazole in both protonation states were derived from different QC ESP (Hartree-Fock (HF), Becke( $1/2$ ) and B3LYP) using the RESP procedure as described in Chapter 2.7. For each of the three QC methods I applied the 6-31G\*\* and 6-31++G\*\* basis set.



	imidazole cation			imidazole		
	6-31G**			6-31++G**		
	HF	Becke $^{1/2}$	B3LYP	HF	Becke $^{1/2}$	B3LYP
H <sub>N1</sub>	0.3701	0.3629	0.3510			
N	-0.1557	-0.1215	-0.1035	0.3171	0.3070	0.2907
C <sub>1</sub>	0.0751	0.0333	0.0243	-0.2492	-0.2171	-0.1951
H <sub>C1</sub>	0.2371	0.2284	0.2184	0.2246	0.1954	0.1861
N <sub>2</sub>	-0.1561	-0.1219	-0.1039	0.1054	0.0937	0.0839
H <sub>N2</sub>	0.3701	0.3629	0.3511	-0.5442	-0.5088	-0.4914
C <sub>3</sub>	-0.1123	-0.1019	-0.0863	0.1631	0.1547	0.1572
H <sub>C3</sub>	0.2422	0.2301	0.2177	0.0938	0.0829	0.0722
C <sub>4</sub>	-0.1127	-0.1023	-0.0867	-0.3179	-0.2978	-0.2771
H <sub>C4</sub>	0.2422	0.2301	0.2178	0.2072	0.1890	0.1736
	6-31++G**			6-31++G**		
	HF	Becke $^{1/2}$	B3LYP	HF	Becke $^{1/2}$	B3LYP
H <sub>N1</sub>	0.3666	0.3608	0.3493			
N	-0.1441	-0.1169	-0.1018	0.3118	0.3021	0.2868
C <sub>1</sub>	0.0692	0.0290	0.0235	-0.2302	-0.2033	-0.1877
H <sub>C1</sub>	0.2359	0.2292	0.2188	0.2335	0.2170	0.2147
N <sub>2</sub>	-0.1445	-0.1172	-0.1022	0.1031	0.0898	0.0792
H <sub>N2</sub>	0.3666	0.3608	0.3494	-0.5653	-0.5471	-0.5362
C <sub>3</sub>	-0.1162	-0.1043	-0.0872	0.1871	0.1937	0.0663
H <sub>C3</sub>	0.2416	0.2316	0.2189	0.08991	0.0774	0.2004
C <sub>4</sub>	-0.1167	-0.1047	-0.0876	-0.3430	-0.3279	-0.3052
H <sub>C4</sub>	0.2416	0.2316	0.2189	0.2129	0.1983	0.1817

## Appendix B

### Abbreviations used in the text:

AcN, acetonitrile

AcN/DMAc, aprotic solvents AcN and DMAc

bc1,

b6f,

B3LYP functional, Becke 3 Lee, Yang and Parr functional

Becke(<sup>1</sup>/<sub>2</sub>), Becke-half&half

CBS, complete basis set

CHARMM, Chemistry at Harvard macromolecular mechanics

CPCM, cosmo polarized continuum model

CPU, central processor unit

DFT, density functional theory

DNA, desoxyribonucleic acid

B3LYP, density functional theory used in combination with the B3LYP functional

DMAc, N,N-dimethylacetamide

EA, electron affinity

ESP, electrostatic potential

$E^{\circ}_{\text{redox}}$ , standard redox potential

G3MP2, Gaussian3-MP2

His, histidine

LPBE, linearized Poisson-Boltzmann equation

MEAD, macroscopic electrostatics with atomic detail

MP2, second-order Møller Plesset

MP4, fourth-order Møller Plesset

NHE, normal hydrogen electrode

NIST, National Institute of Standards and Technology

PA, proton affinity

PBE, Poisson-Boltzmann equation

*p*-benzoquinones, para-benzoquinone

PCM, polarized continuum model

PSII,

PSI,

QC, quantum chemical

QCISD, quadratic configuration interaction

RESP, restrained electrostatic potential

RMS deviation, root mean square deviation

SCE, standard calomel electrode

SHE, standard hydrogen electrode

TVR contribution, translational rotational vibrational contribution

vdW, van-der-Waals

ZPVE, zero point vibrational energy



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## Publications

### Journal articles:

1. **M. Schmidt am Busch and E.W. Knapp (2004).** Accurate  $pK_a$  determination for a heterogeneous group of organic molecules. *ChemPhysChem*, **5**, 1513-1522.
2. **M. Schmidt am Busch and E.W. Knapp (2005).** One-electron reduction potential for oxygen- and sulfur centered organic radicals in protic and aprotic solvents. *J. Am Chem. Soc.*, **127**, 15730-15737.
3. **H. Kress, A. Jarrin, E. Thuroff, R. Saunders, C. Weise, M. Schmidt am Busch, E.W. Knapp, M. Wedde and A. Vilcinskas (2004).** A Kunitz type protease inhibitor related protein is synthesized in *Drosophila* prepupal salivary glands and released into the moulting fluid during pupation. *Insect Biochemistry and Molecular Biology*, **34**, 855-869.

## Acknowledgements

This thesis was prepared in the group of Professor Ernst-Walter Knapp at the Freie Universität Berlin. I would like to express my thanks to all people who helped and supported me during my PhD work. Especially I would like to thank my supervisor Professor Ernst-Walter Knapp for giving me the opportunity to work as a PhD student in his group. Also I would like to express my thanks for his constant interest and ongoing support for my research efforts.

Special thanks to Professor Dr. Matthias Ullmann, whom I met in Heidelberg in the year 2001 and who recommended me to my advisor Professor Ernst-Walter Knapp.

I would like to thank Artur Galstjan and Björn Kolbeck for their efforts to keep the computer in the laboratory running.

I would like to thank Dr. Thomas Renger and Julia Adolphs who carefully read parts of this thesis.

Special thanks to my parents for their constant support.