Supplementary Information for "Atomic Forces for Geometry-Dependent Point Multipole and Gaussian Multipole Models" by D.M. Elking et al.

Additional Results

Introduction

In this section of the Supplementary Information, additional results for static and geometry-dependent Gaussian multipoles fit to the electrostatic potential (ESP) calculated at the HF/6-31G* and HF/aug-cc-pVTZ levels are presented. Electrostatic energies, atomic forces, molecular forces, and molecular torques calculated by Gaussian multipoles for hydrogen bonded dimers are compared to their respective ab initio reference values. In addition, it is shown that atomic forces are independent of local reference frame definition for geometry-dependent multipole models, but not for static multipole models. Lastly, the error in molecular multipole moment calculated by static and geometry-dependent multipoles is plotted as a function of bond length and bond angle for the case of water.

Electrostatic Energy

Electrostatic energies calculated by Gaussian multipoles for hydrogen bonded dimers are compared to their ab initio reference values. In Tables SI.1 and SI.2, electrostatic energies are given for Gaussian multipoles fit to the ESP calculated at the HF/6-31G* and HF/aug-cc-pVTZ levels, respectively. Note that examples taken from Table SI.1 have been used to form Table 1 of the main text. There is a significant improvement in going from Gaussian monopoles to Gaussian quadrupoles, while there is only a small increase in accuracy in going from Gaussian quadrupoles to Gaussian hexadecapoles. The rmsd errors in electrostatic energy with respect to ab initio are 0.631, 0.546, 0.085, 0.095, and 0.067 kcal/mol for HF/6-31G* Gaussian monopoles, dipoles, quadrupoles, octapoles, and hexadecapoles, respectively. For HF/aug-cc-pVTZ Gaussian multipoles, the rmsd errors in energy are 0.900, 0.395, 0.168, 0.068, and 0.097 kcal/mol for Gaussian monopoles, dipoles, quadrupoles, octapoles, and hexadecapoles, respectively.

Table SI.1 Electrostatic energies (kcal/mol) of X – water dimers for HF/6-31G* Gaussian monopoles (E_{M}), dipoles (E_{MD}), quadrupoles (E_{MDQ}), octapoles (E_{MDQO}), and hexadecapoles (E_{MDQOH}) are compared to the reference ab initio RVS[67,68] values E_{QM}.

X	E_{M}	E_{MD}	E_{MDQ}	E_{MDQO}	E_{MDQOH}	E_{QM} (RVS)
Water$^{(1)}$[a]	-6.845	-7.074	-7.502	-7.520	-7.542	-7.546
Water$^{(2)}$	-4.463	-4.361	-4.535	-4.551	-4.578	-4.582
Water$^{(3)}$	-3.649	-3.299	-3.257	-3.265	-3.276	-3.283
Methanol$^{(1)}$	-7.172	-6.735	-7.238	-7.257	-7.285	-7.265
Methanol$^{(2)}$	-6.335	-7.013	-7.502	-7.532	-7.567	-7.561
Formamide$^{(1)}$	-11.35	-11.18	-11.75	-11.78	-11.86	-11.98
Formamide$^{(2)}$	-7.654	-7.461	-8.080	-8.029	-7.995	-8.108
Formamide$^{(3)}$	-6.769	-6.539	-6.990	-7.00	-7.056	-7.053
NMF	-8.598	-7.919	-8.286	-8.366	-8.346	-8.409
Ammonia	-8.594	-9.130	-9.982	-10.06	-10.07	-10.03
Acetylaldehyde$^{(1)}$	-6.808	-6.221	-6.849	-6.879	-6.922	-7.022
Acetylaldehyde$^{(2)}$	-6.057	-5.810	-6.532	-6.399	-6.439	-6.550
Formaldehyde	-5.872	-5.484	-6.087	-5.903	-6.014	-6.113
Dimethyl Ether	-5.791	-6.438	-6.744	-6.828	-6.840	-6.787
Fluoromethane	-4.143	-3.841	-4.048	-4.015	-4.031	-4.096
Chloromethane	-2.928	-3.638	-3.402	-3.369	-3.355	-3.415
Difluromethane	-2.305	-2.682	-2.733	-2.755	-2.780	-2.803
rmsd	0.631	0.546	0.085	0.095	0.067	

[a] The superscripts $^{(1),(2),(3)}$ denote multiple geometries of a given dimer.

Table SI.2 Electrostatic energies (kcal/mol) of X – water dimers for HF/aug-cc-pVTZ Gaussian monopoles (E_{M}), dipoles (E_{MD}), quadrupoles (E_{MDQ}), octapoles (E_{MDQO}), and hexadecapoles (E_{MDQOH}) are compared to the reference ab initio RVS[67,68] values E_{QM}.

X	E_{M}	E_{MD}	E_{MDQ}	E_{MDQO}	E_{MDQOH}	E_{QM} (RVS)
Water$^{(1)}$[a]	-7.495	-7.418	-7.982	-7.694	-7.775	-7.748
Water$^{(2)}$	-4.482	-4.296	-4.511	-4.588	-4.547	-4.630
Water$^{(3)}$	-3.268	-2.684	-2.634	-2.671	-2.668	-2.733
Methanol$^{(1)}$	-9.238	-8.183	-8.851	-8.577	-8.635	-8.726
Methanol$^{(2)}$	-6.421	-7.172	-7.719	-7.627	-7.727	-7.704
Ammonia$^{(1)}$	-8.493	-9.943	-11.02	-10.75	-10.63	-10.75
Ammonia$^{(2)}$	-3.426	-3.322	-3.602	-3.563	-3.558	-3.615
Formaldehyde	-7.753	-7.017	-7.718	-7.445	-7.320	-7.359
Difluromethane$^{(1)}$	-3.109	-2.352	-2.276	-2.212	-2.358	-2.176
Difluromethane$^{(2)}$	-2.956	-3.381	-3.514	-3.543	-3.550	-3.623
Fluoromethane$^{(1)}$	-3.906	-3.490	-3.279	-3.160	-3.316	-3.138
Fluoromethane$^{(2)}$	-1.703	-2.137	-2.194	-2.192	-2.161	-2.222
rmsd	0.900	0.395	0.168	0.068	0.097	

[a] The superscripts $^{(1),(2),(3)}$ denote multiple geometries of a given dimer.

Atomic Forces

Atomic electrostatic forces on hydrogen bonded dimers are calculated by static and geometry-dependent Gaussian multipoles and compared to their reference ab initio values. In Table SI.3, the electrostatic atomic forces calculated by static and geometry-dependent HF/6-31G* Gaussian octapoles on a methanol molecule in a methanol-water dimer are compared to their reference HF/6-31G* electrostatic atomic forces. For all atoms, the atomic forces calculated by geometry-dependent octapoles reproduce the ab initio force significantly better than static Gaussian octapoles. For example, the ab initio electrostatic force on carbon (C) is $\mathbf{F}^{\text{ab initio}}$ = (3.689, -6.618, 0.495) kcal/mol/ Å, which can be compared to the forces calculated by static Gaussian octapoles of $\mathbf{F}^{\text{static}}$ = (5.124, -5.253, 1.646) kcal/mol/ Å and geometry-dependent Gaussian octapoles of $\mathbf{F}^{\text{geom. depend.}}$ = (3.580, -6.589, 0.473). The rmsd errors in atomic force with respect to ab initio over all atoms in the methanol-water dimer are 0.135 and 1.450 kcal/mol/Å for geometry-dependent and static Gaussian octapoles, respectively.

Table SI.3 Atomic electrostatic forces (kcal/mol/Å) on methanol in the methanol-water(1) dimer calculated by static and geometry-dependent HF/6-31G* Gaussian octapoles.

F(C)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{static}}$	5.124	-5.253	1.646
$\mathbf{F}^{\text{geom. depend.}}$	3.580	-6.589	0.473
$\mathbf{F}^{\text{ab initio}}$	3.689	-6.618	0.495

F(O)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{static}}$	-15.98	-1.669	-0.100
$\mathbf{F}^{\text{geom. depend.}}$	-14.69	0.022	1.132
$\mathbf{F}^{\text{ab initio}}$	-14.33	0.045	1.028

F(H-O)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{static}}$	0.347	0.763	0.768
$\mathbf{F}^{\text{geom. depend.}}$	-0.307	0.764	0.154
$\mathbf{F}^{\text{ab initio}}$	-0.346	0.777	0.173

F(H1-C)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{static}}$	-0.569	0.888	0.090
$\mathbf{F}^{\text{geom. depend.}}$	0.138	0.151	0.288
$\mathbf{F}^{\text{ab initio}}$	0.037	0.181	0.300

F(H2-C)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{static}}$	-1.108	0.379	-0.179
$\mathbf{F}^{\text{geom. depend.}}$	-1.186	1.090	-0.221
$\mathbf{F}^{\text{ab initio}}$	-1.138	1.162	-0.220

F(H3-C)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{static}}$	-0.658	1.278	-1.281
$\mathbf{F}^{\text{geom. depend.}}$	-0.387	0.946	-0.883
$\mathbf{F}^{\text{ab initio}}$	-0.478	0.933	-0.897

[a] The rmsd error in atomic force with respect to ab initio over all atoms is 0.135 and 1.450 kcal/mol/Å for geometry-dependent and static Gaussian multipoles, respectively.

The rmsd error in electrostatic atomic force with respect to ab initio is calculated for the other hydrogen bonded dimers and presented in Tables SI.4 and SI.5 for HF/6-31G* and HF/aug-cc-pVTZ Gaussian multipoles, respectively. Note that Table 4 of the main text has been formed from examples of Table SI.4. In all cases, the errors in atomic force for geometry-dependent Gaussian multipoles are significantly smaller than the errors for static Gaussian multipoles. The rmsd errors averaged over all molecules are 0.877, 0.265, 0.124, and 0.113 kcal/mol/Å for geometry-dependent HF/6-31G*

Gaussian dipoles, quadrupoles, octapoles, and hexadecapoles, respectively. For geometry-dependent HF/aug-cc-pVTZ Gaussian multipoles, the average rmsd errors are 0.914, 0.306, 0.167, and 0.118 kcal/mol/Å for geometry-dependent Gaussian dipoles, quadrupoles, octapoles, and hexadecapoles, respectively.

Table SI.4 rmsd error in electrostatic atomic forces (kcal/mol/Å) with respect to ab initio of X-water dimers for static and geometry-dependent HF/6-31G* Gaussian dipoles (ΔF_{MD}), quadrupoles (ΔF_{MDQ}), octapoles (ΔF_{MDQO}), and hexadecapoles ($\Delta F_{\mathrm{MDQOH}}$).[a]

X	Geometry-Dependent				Static			
	ΔF_{MD}	ΔF_{MDQ}	ΔF_{MDQO}	$\Delta F_{\mathrm{MDQOH}}$	ΔF_{MD}	ΔF_{MDQ}	ΔF_{MDQO}	$\Delta F_{\mathrm{MDQOH}}$
Water$^{(1)}$,[b]	1.287	0.449	0.147	0.155	3.913	1.634	1.567	0.991
Water$^{(2)}$	0.284	0.090	0.052	0.044	3.231	1.063	0.928	0.671
Water$^{(3)}$	0.094	0.036	0.042	0.032	2.879	0.901	0.786	0.512
Methanol$^{(1)}$	1.089	0.381	0.135	0.149	2.734	1.543	1.450	1.030
Methanol$^{(2)}$	1.131	0.333	0.146	0.145	2.959	2.124	1.279	0.990
Formamide$^{(1)}$	1.239	0.315	0.168	0.135	4.239	4.346	3.354	2.722
Formamide$^{(2)}$	1.206	0.326	0.129	0.143	3.415	3.549	2.780	1.812
Formamide$^{(3)}$	0.760	0.189	0.213	0.086	3.961	2.007	1.485	1.878
NMF	0.853	0.316	0.115	0.118	3.166	2.616	2.285	2.125
Ammonia	1.660	0.446	0.153	0.203	4.849	2.137	2.000	1.432
Acetylaldehyde$^{(1)}$	1.011	0.312	0.127	0.122	2.266	2.792	2.837	1.758
Acetylaldehyde$^{(2)}$	1.020	0.273	0.126	0.111	2.240	2.980	3.143	1.786
Formaldehyde	1.166	0.312	0.208	0.138	2.308	3.199	2.680	1.603
Dimethyl Ether	0.917	0.331	0.122	0.129	1.845	1.406	2.162	2.188
Fluoromethane	0.624	0.224	0.123	0.135	1.605	1.531	1.207	0.692
Chloromethane	0.369	0.084	0.058	0.041	2.099	1.443	1.521	0.902
Difluromethane	0.197	0.092	0.048	0.032	1.403	0.971	0.829	0.612
Average	0.877	0.265	0.124	0.113	2.889	2.132	1.900	1.394

[a] Gaussian monopoles have been omitted for brevity.

[b] The superscripts $^{(1),(2),(3)}$ denote multiple geometries of a given dimer.

Table SI.5 rmsd error in electrostatic atomic forces (kcal/mol/Å) with respect to ab initio of X-water dimers for static and geometry-dependent HF/aug-cc-pVTZ Gaussian dipoles (ΔF_{MD}), quadrupoles (ΔF_{MDQ}), octapoles (ΔF_{MDQO}), and hexadecapoles (ΔF_{MDQOH}).[a]

X	Geometry-Dependent				Static			
	ΔF_{MD}	ΔF_{MDQ}	ΔF_{MDQO}	ΔF_{MDQOH}	ΔF_{MD}	ΔF_{MDQ}	ΔF_{MDQO}	ΔF_{MDQOH}
Water$^{(1),b}$	1.439	0.448	0.209	0.101	3.885	3.375	10.52	11.52
Water$^{(2)}$	0.521	0.234	0.153	0.089	2.836	2.001	6.551	7.126
Water$^{(3)}$	0.181	0.106	0.057	0.050	2.494	1.569	5.197	5.585
Methanol$^{(1)}$	1.525	0.425	0.205	0.113	2.612	2.966	7.955	9.186
Methanol$^{(2)}$	1.352	0.333	0.172	0.049	2.923	2.302	7.010	8.310
Ammonia$^{(1)}$	1.834	0.571	0.270	0.129	5.204	4.267	11.15	11.42
Ammonia$^{(2)}$	1.015	0.176	0.129	0.059	3.166	1.938	2.789	3.274
Formaldehyde	1.636	0.506	0.299	0.142	2.528	4.536	7.055	7.047
Difluromethane$^{(1)}$	0.261	0.148	0.157	0.281	1.140	1.260	2.623	2.671
Difluromethane$^{(2)}$	0.480	0.334	0.183	0.121	2.082	1.127	2.453	3.105
Fluoromethane$^{(1)}$	0.387	0.166	0.096	0.218	1.564	1.495	4.135	4.350
Fluoromethane$^{(2)}$	0.345	0.236	0.082	0.075	1.780	1.393	2.054	2.214
Average	0.914	0.306	0.167	0.118	2.684	2.352	5.791	6.317

[a] Gaussian monopoles have been omitted for brevity.

[b] The superscripts $^{(1),(2),(3)}$ denote multiple geometries of a given dimer.

Total Molecular Force and Total Molecular Torque

Total molecular forces and total molecular torques for static Gaussian multipoles are calculated for the set of hydrogen bonded dimers and compared to their ab initio reference values. Recall that the geometry-dependent contribution to total molecular force and total molecular torque is zero (at equilibrium monomer geometries). In Table SI.6, the total molecular force on a dimethyl ether molecule in a dimethyl ether-water dimer is given. The molecular electrostatic force on dimethyl ether calculated by static Gaussian octapoles is (-12.610, 0.003, 1.230) kcal/mol/Å, which can be compared to the ab initio result of (-12.200, 0.003, 1.162) kcal/mol/Å. The rmsd error in total molecular force in the dimethyl-ether water dimer is 0.238 kcal/mol/Å.

Table SI.6 Total Molecular Force (kcal/mol/Å) on Dimethyl Ether in a Dimethyl Ether-Water Dimer[a]

	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
Gauss. Oct.	-12.610	0.003	1.230
Ab initio	-12.200	0.003	1.162

[a] Calculated by HF/6-31G* Gaussian octapoles. The rmsd error in total molecular force is 0.239 kcal/mol/Å.

The rmsd errors in molecular force are calculated for the other hydrogen bonded dimers and presented in Tables SI.7 and SI.8 for static HF/6-31G* and HF/aug-cc-pVTZ Gaussian multipoles, respectively. The rmsd errors averaged over all dimers are 0.751, 0.549, 0.124, 0.115, and 0.081 kcal/mol/Å for static HF/6-31G* Gaussian monopoles, dipoles, quadrupoles, octapoles, and hexadecapoles. For HF/aug-cc-pVTZ Gaussian multipoles, the average rmsd errors are 1.222, 0.316, 0.453, 0.140, and 0.142 kcal/mol/Å for Gaussian monopoles, dipoles, quadrupoles, octapoles, and hexadecapoles.

Table SI.7 rmsd error in electrostatic total *molecular* forces (kcal/mol/Å) with respect to ab initio of X-water dimers for HF/6-31G* Gaussian[a] monopoles ($\Delta\boldsymbol{F}_{\mathrm{M}}$), dipoles ($\Delta\boldsymbol{F}_{\mathrm{MD}}$), quadrupoles ($\Delta\boldsymbol{F}_{\mathrm{MDQ}}$), octapoles ($\Delta\boldsymbol{F}_{\mathrm{MDQO}}$), and hexadecapoles ($\Delta\boldsymbol{F}_{\mathrm{MDQOH}}$).

X	$\Delta\boldsymbol{F}_{\mathrm{M}}$	$\Delta\boldsymbol{F}_{\mathrm{MD}}$	$\Delta\boldsymbol{F}_{\mathrm{MDQ}}$	$\Delta\boldsymbol{F}_{\mathrm{MDQO}}$	$\Delta\boldsymbol{F}_{\mathrm{MDQOH}}$
Water(1),[b]	0.305	0.341	0.151	0.155	0.168
Water(2)	0.162	0.258	0.096	0.067	0.002
Water(3)	0.337	0.031	0.067	0.051	0.017
Methanol(1)	1.359	0.394	0.193	0.177	0.202
Methanol(2)	1.198	0.471	0.151	0.171	0.205
Formamide(1)	0.550	0.846	0.066	0.238	0.177
Formamide(2)	1.203	0.715	0.238	0.126	0.081
Formamide(3)	0.132	0.661	0.070	0.032	0.049
NMF	1.519	0.564	0.146	0.236	0.100
Ammonia	0.630	0.945	0.080	0.071	0.052
Acetylaldehyde(1)	0.821	0.845	0.053	0.144	0.076
Acetylaldehyde(2)	0.737	0.788	0.229	0.086	0.058
Formaldehyde	0.927	0.656	0.180	0.188	0.071
Dimethyl Ether	0.292	0.280	0.162	0.239	0.250
Fluoromethane	1.122	0.291	0.045	0.057	0.019
Chloromethane	0.574	0.532	0.030	0.041	0.045
Difluromethane	0.466	0.214	0.090	0.043	0.010
Average	0.751	0.549	0.124	0.115	0.081

[a] At equilibrium monomer geometries, the geometry-dependent contribution to the total molecular force is zero.

[b] The superscripts (1),(2),(3) denote multiple geometries of a given dimer.

Table SI.8 rmsd error in electrostatic total *molecular* forces (kcal/mol/Å) with respect to ab initio of X-water dimers for static and geometry-dependent HF/aug-cc-pVTZ Gaussian[a] monopoles ($\Delta \boldsymbol{F}_{\mathrm{M}}$), dipoles ($\Delta \boldsymbol{F}_{\mathrm{MD}}$), quadrupoles ($\Delta \boldsymbol{F}_{\mathrm{MDQ}}$), octapoles ($\Delta \boldsymbol{F}_{\mathrm{MDQO}}$), and hexadecapoles ($\Delta \boldsymbol{F}_{\mathrm{MDQOH}}$).

X	$\Delta \boldsymbol{F}_{\mathrm{M}}$	$\Delta \boldsymbol{F}_{\mathrm{MD}}$	$\Delta \boldsymbol{F}_{\mathrm{MDQ}}$	$\Delta \boldsymbol{F}_{\mathrm{MDQO}}$	$\Delta \boldsymbol{F}_{\mathrm{MDQOH}}$
Water(1),[b]	1.214	0.071	0.820	0.078	0.061
Water(2)	0.359	0.202	0.085	0.203	0.042
Water(3)	0.429	0.032	0.049	0.053	0.029
Methanol(1)	2.757	0.307	0.766	0.194	0.102
Methanol(2)	1.145	0.379	0.405	0.087	0.043
Difluromethane(1)	2.201	0.480	0.377	0.202	0.485
Fluoromethane(1)	2.278	0.739	0.429	0.109	0.397
Difluromethane(2)	0.195	0.226	0.083	0.152	0.110
Fluoromethane(2)	0.416	0.097	0.068	0.062	0.026
Ammonia(1)	0.901	0.467	1.059	0.095	0.233
Ammonia(2)	0.398	0.180	0.203	0.052	0.022
Formaldehyde	2.375	0.617	1.096	0.399	0.165
Average	1.222	0.316	0.453	0.140	0.142

[a] At equilibrium monomer geometries, the geometry-dependent contribution to the total molecular torque is zero.

[b] The superscripts (1),(2),(3) denote multiple geometries of a given dimer.

For the water-water(1) dimer, the error in molecular force for HF/aug-cc-pVTZ Gaussian dipoles of 0.071 kcal/mol/Å is significantly smaller than the corresponding error for HF/aug-cc-pVTZ Gaussian quadrupoles of 0.820 kcal/mol/Å. This result is unexpected since the errors in atomic force for geometry-dependent HF/aug-cc-pVTZ Gaussian dipoles and quadrupoles are 1.439 and 0.448 kcal/mol/Å, respectively (from Table SI.5). In order to see why the error in molecular force for Gaussian dipoles is smaller than usual, the individual atomic forces for one of the water molecules in the water-water(1) dimer are given in Table SI.9 for geometry-dependent Gaussian dipoles, quadrupoles, and octapoles.

Table SI.9 Atomic electrostatic forces (kcal/mol/Å) on a water in the water-water(1) dimer calculated by geometry-dependent HF/aug-cc-pVTZ Gaussian dipoles, quadrupoles, and octapoles.

F(O)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{Gauss. Dip.}}$	0.136	0.378	0.002
$\mathbf{F}^{\text{Gauss. Quad.}}$	-0.168	3.678	0.002
$\mathbf{F}^{\text{Gauss. Oct.}}$	-0.390	5.185	0.002
$\mathbf{F}^{\text{ab initio}}$	-0.328	4.747	0.002

F(H1)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{Gauss. Dip.}}$	-0.231	-13.35	-0.003
$\mathbf{F}^{\text{Gauss. Quad.}}$	-0.047	-17.73	-0.004
$\mathbf{F}^{\text{Gauss. Oct.}}$	0.077	-17.89	-0.004
$\mathbf{F}^{\text{ab initio}}$	-0.156	-17.50	-0.004

F(H2)	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$
$\mathbf{F}^{\text{Gauss. Dip.}}$	-0.884	-0.967	0.000
$\mathbf{F}^{\text{Gauss. Quad.}}$	-0.784	-1.193	0.000
$\mathbf{F}^{\text{Gauss. Oct.}}$	-0.594	-1.113	0.000
$\mathbf{F}^{\text{ab initio}}$	-0.556	-1.078	0.000

rmsd
1.439
0.448
0.209

The molecular force on water can be found by summing the atomic forces for the three atoms and is given in Table SI.10. Coincidently, HF/aug-cc-pVTZ Gaussian dipoles predict a better molecular force on water than Gaussian quadrupoles, but Gaussian quadrupoles predict better atomic forces. Thus, the small error in molecular force Gaussian dipoles is due to a cancelation of error. A similar argument can be made for the other dimers in Table SI.8 for which the error in molecular force for Gaussian quadrupoles is larger than the error for Gaussian dipoles.

Table SI.10 Total Molecular Force (kcal/mol/Å) on a water in the water-water(1) dimer.

	$\mathbf{F}_x$	$\mathbf{F}_y$	$\mathbf{F}_z$	rmsd
Gauss. Dip.	-0.979	-13.94	-0.001	0.071
Gauss. Quad.	-0.998	-15.25	-0.002	0.820
Gauss. Oct.	-0.907	-13.81	-0.002	0.078
Ab initio	-1.041	-13.83	-0.002	

[a] Calculated by HF/aug-cc-pVTZ Gaussian dipoles, quadrupoles, and octapoles.

The molecular torques with respect to the center of mass (COM) are calculated for static Gaussian multipoles and compared to their reference ab initio values calculated from electrostatic atomic forces. In Table SI.11, the molecular torque on formaldehyde in a formaldehyde-water dimer is given for static HF/6-31G* Gaussian octapoles. For static HF/6-31G* Gaussian octapoles, the molecular torque $\boldsymbol{\tau}$ is (0.00, 0.00, 4.86) kcal/mol which can be compared to the ab initio result of (0.00, 0.00, 4.48) kcal/mol. The rmsd error in molecular torque in the formaldehyde-water dimer is 0.155 kcal/mol.

Table SI.11 Total Molecular Torque on Formaldehyde in a Formaldehyde-Water Dimer[a,b] (kcal/mol)

	$\boldsymbol{\tau}_x$	$\boldsymbol{\tau}_y$	$\boldsymbol{\tau}_z$
Gauss. Oct.	0.000	0.000	4.860
Ab initio	0.000	0.000	4.480

[a] Torque is calculated with respect to the center of mass (COM) by HF/6-31G* Gaussian octapoles.
[b] The rmsd error in total molecular torque is 0.155 kcal/mol.

The rmsd errors in molecular torque are calculated for the other hydrogen bonded dimers and given in Tables SI.12 and SI.13 for HF/6-31G* and HF/aug-cc-pVTZ Gaussian multipoles, respectively. The rmsd errors in molecular torque averaged over the hydrogen bonded dimers are 0.726, 0.489, 0.096, 0.127, 0.069 kcal/mol for static HF/6-31G* Gaussian monopoles, dipoles, quadrupoles, octapoles, and hexadecapoles, repectively. For static HF/aug-cc-pVTZ Gaussian multipoles, the average rmsd errors are 0.556, 0.253, 0.150, 0.107, and 0.068 kcal/mol for Gaussian monopoles, dipoles, quadrupoles, octapoles, and hexadecapoles, respectively.

Table SI.12 rmsd error in electrostatic total *molecular* torque[a] (kcal/mol) with respect to ab initio of X-water dimers for HF/6-31G* Gaussian monopoles ($\Delta\mathbf{\Gamma}_{\mathrm{M}}$), dipoles ($\Delta\mathbf{\Gamma}_{\mathrm{MD}}$), quadrupoles ($\Delta\mathbf{\Gamma}_{\mathrm{MDQ}}$), octapoles ($\Delta\mathbf{\Gamma}_{\mathrm{MDQO}}$), and hexadecapoles ($\Delta\mathbf{\Gamma}_{\mathrm{MDQOH}}$).

X	$\Delta\mathbf{\Gamma}_{\mathrm{M}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MD}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MDQ}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MDQO}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MDQOH}}$
Water(1),[b,c]	0.347	0.172	0.024	0.024	0.044
Methanol(1)	0.728	0.267	0.080	0.101	0.138
Methanol(2)	0.523	0.252	0.033	0.075	0.099
Formamide(1)	1.950	0.758	0.096	0.394	0.235
Formamide(2)	0.900	1.055	0.167	0.172	0.084
Formamide(3)	0.314	0.445	0.089	0.052	0.001
NMF	1.895	0.591	0.304	0.418	0.221
Ammonia	0.878	0.351	0.005	0.015	0.030
Acetylaldehyde(1)	0.924	0.896	0.027	0.222	0.154
Acetylaldehyde(2)	0.731	0.875	0.241	0.153	0.029
Formaldehyde	0.724	0.737	0.193	0.155	0.027
Dimethyl Ether	0.428	0.447	0.016	0.079	0.044
Fluoromethane	0.776	0.178	0.092	0.115	0.010
Chloromethane	0.844	0.810	0.026	0.109	0.071
Difluromethane	0.086	0.067	0.026	0.009	0.008
Average	0.726	0.489	0.096	0.127	0.069

[a] Torque is calculated with respect to the center of mass (COM).

[b] The superscripts (1),(2),(3) denote multiple geometries of a given dimer.

[c] The total molecular torque on the water-water(2) and water-water(3) dimers are zero because of symmetry.

Table SI.13 rmsd error in electrostatic total *molecular* torque[a] (kcal/mol) with respect to ab initio of X-water dimers for HF/aug-cc-pVTZ Gaussian monopoles ($\Delta\mathbf{\Gamma}_{\mathrm{M}}$), dipoles ($\Delta\mathbf{\Gamma}_{\mathrm{MD}}$), quadrupoles ($\Delta\mathbf{\Gamma}_{\mathrm{MDQ}}$), octapoles ($\Delta\mathbf{\Gamma}_{\mathrm{MDQO}}$), and hexadecapoles ($\Delta\mathbf{\Gamma}_{\mathrm{MDQOH}}$).

X	$\Delta\mathbf{\Gamma}_{\mathrm{M}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MD}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MDQ}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MDQO}}$	$\Delta\mathbf{\Gamma}_{\mathrm{MDQOH}}$
Water$^{(1),b,c}$	0.551	0.151	0.084	0.113	0.053
Methanol$^{(1)}$	1.368	0.491	0.303	0.216	0.090
Methanol$^{(2)}$	0.741	0.104	0.320	0.138	0.038
Difluromethane$^{(1)}$	0.666	0.150	0.116	0.101	0.140
Fluoromethane$^{(1)}$	0.056	0.132	0.059	0.039	0.022
Difluromethane$^{(2)}$	0.201	0.075	0.000	0.059	0.028
Fluoromethane$^{(2)}$	0.076	0.012	0.034	0.031	0.008
Ammonia$^{(1)}$	1.018	0.356	0.107	0.140	0.089
Ammonia$^{(2)}$	0.284	0.201	0.108	0.098	0.036
Formaldehyde	1.717	1.366	0.677	0.360	0.319
Average	0.556	0.253	0.150	0.107	0.068

[a] Torque is calculated with respect to the center of mass (COM).

[b] The superscripts $^{(1),(2),(3)}$ denote multiple geometries of a given dimer.

[c] The total molecular torque on the water-water$^{(2)}$ and water-water$^{(3)}$ dimers are zero because of symmetry.

Multiple Local Frame Definitions

In static multipole models, the total atomic force is the sum of the orientational + translational atomic forces. The orientational force depends on how the local reference frames are defined. Different definitions of the local reference frame give rise to different orientational forces, which give rise to different total atomic forces for static multipole models. However, for geometry-dependent multipoles, the total orientational + geometry-dependent force is independent of how the local reference frame is defined. In order to show this, a separate calculation requiring increased Gaussian multipole parameter precision is performed on the ammonia-water dimer for different definitions of local reference on the nitrogen in ammonia. For this calculation, the Gaussian multipoles are fit to the ESP on 'extra fine' grids and the finite difference step sizes *h* for calculating $\partial Q_{lm'}^{a,Loc} / \partial \eta_0$ are taken to be 0.001 Å and 0.1° for bond lengths and bond angles, respectively.

In Table SI.14, the atomic orientational force on a nitrogen atom in an ammonia-water dimer calculated by static Gaussian quadrupoles is given for different definitions of the local reference frame on nitrogen in terms of its neighboring hydrogens. As shown, the different definitions of local reference frame give significantly different orientational forces. For example, if the local frame on nitrogen is defined in terms of the H1 and H2 hydrogens, the *x*-component of the orientational force is -1.186 kcal/mol/Å. However, if the local frame for nitrogen is defined in terms of the H1 and H3 hydrogens, the *x*-component of the orientational force is -2.938 kcal/mol/Å.

If the geometry dependence of the atomic multipoles is accounted for, the total orientational + geometry-dependent force is the same for all definitions of the local reference frame. In Table SI.15, the atomic orientational + geometry-dependent force on nitrogen in the ammonia-water dimer is given for different definition of the local reference frame on nitrogen. The total orientational + geometry-dependent atomic forces agree to a precision of 10^{-4}. For example, if the local frame on nitrogen is defined in terms of the H1 and H2 hydrogens, then the orientational + geometry-dependent force on nitrogen is (-3.5831, -1.1863, 0.0270) kcal/mol/Å. If the local frame on nitrogen is defined in terms of the H1 and H3 hydrogens, then the orientational+geometry-dependent force on nitrogen is (-3.5832, -1.1863, 0.0270) kcal/mol/Å. The agreement of the orientational + geometry-dependent forces to a precision of 10^{-4} is mainly due to the precision of the optimized Gaussian multipole parameters $Q_{lm'}^{a,Loc}$ (10^{-8}) and its finite difference derivatives $\partial Q_{lm'}^{a,Loc} / \partial \eta$ (10^{-4}) when the multipole parameters are optimized to the ESP on 'extra fine' grids. This result indicates that the total atomic force is independent of local reference frame definition for geometry-dependent multipoles, but not for static multipoles.

Table SI.14 Dependence of Atomic Orientational Force (kcal/mol/Å) on the Choice of Local Frame[a]

N1	N2	F_x	F_y	F_z
H1	H2	-1.186	0.666	-0.000
H1	H3	-2.938	0.039	0.001
H2	H3	-2.787	-0.009	-0.001

[a] Atomic orientational force on the nitrogen atom in an ammonia-water dimer is calculated by HF/6-31G* Gaussian quadrupoles using different definitions of the local reference frames for nitrogen in terms of neighboring hydrogens H1, H2, H3.

Table SI.15 Dependence of Atomic Orientational + Geometry-Dependent Force (kcal/mol/Å) on the Choice of Local Frame[a,b]

N1	N2	X	Y	Z
H1	H2	-3.5831	-1.1863	0.0270
H1	H3	-3.5832	-1.1863	0.0270
H2	H3	-3.5832	-1.1864	0.0269

[a] Atomic orientational + geometry-dependent force on the nitrogen atom in an ammonia-water dimer is calculated by HF/6-31G* Gaussian quadrupoles using different definitions of the local reference frames for nitrogen in terms of neighboring hydrogens H1, H2, H3.

[b] The geometry-dependent Gaussian multipoles are fit on 'extra fine' grids.

Molecular Multipole Moment Dependence on Geometry For Water

In this section, the error in molecular multipole moment calculated by static and geometry-dependent HF/6-31G* Gaussian dipoles and quadrupoles is plotted as a function of bond length and bond angle for a water molecule. The equilibrium HF/6-31G* bond length and bond angle are 0.9473 Å and 105.0°, respectively. In Figure SI.1, the error in molecular dipole moment calculated by static and geometry-dependent Gaussian dipoles is plotted as a function of bond angle (the bond length is kept at is equilibrium value of 0.9473 Å). At the equilibrium bond angle of 105.0°, the HF/6-31G* molecular dipole of water is 2.208 D. Both static and geometry-dependent Gaussian dipoles reproduce the correct molecular dipole, with values of 2.209 D and 2.221 D, respectively. However, the errors in molecular dipole moment increase significantly for static Gaussian dipoles, but not for geometry-dependent Gaussian dipoles as the deviation from equilibrium bond angle increases. Similar results hold for the error in molecular dipole (Figure SI.2), molecular quadrupole (Figure SI.3), and molecular octapole (Figure SI.4) moment of water as a function of bond angle calculated by static and geometry-dependent Gaussian quadrupoles.

In Figure SI.5, similar trends are found for the error in molecular dipole moment as a function of bondlength calculated by static and geometry-dependent Gaussian dipoles. In addition, the error in molecular dipole (Figure SI.6), molecular quadrupole (Figure SI.7), and molecular octapole (Figure SI.8) moment of water as a function of bondlength calculated by static and geometry-dependent Gaussian quadrupoles. Interestingly, static Gaussian quadrupoles give the correct molecular dipole as a function of bondlength (but not bondangle). The errors in molecular dipole calculated by both static and geometry-dependent Gaussian quadrupoles are below 0.03 D for bondlengths between 0.9 and 1.0 Å.

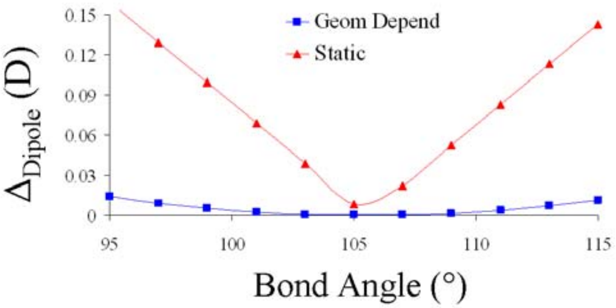

Figure SI.1. Error in molecular dipole moment with respect to ab initio as a function of bondangle for water calculated by static and geometry-dependent HF/6-31G* Gaussian dipoles.

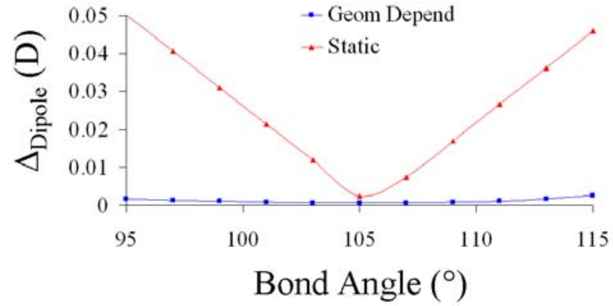

Figure SI.2. Error in molecular dipole moment with respect to ab initio as a function of bondangle for water calculated by static and geometry-dependent HF/6-31G* Gaussian quadrupoles.

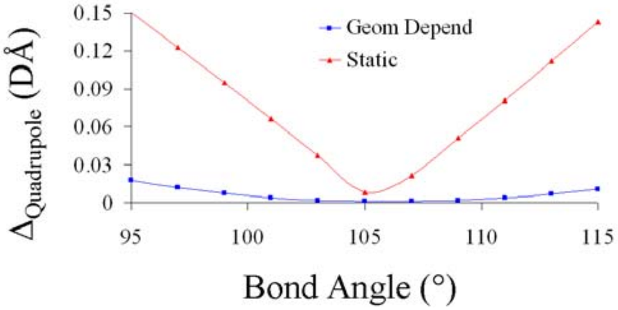

Figure SI.3. Error in molecular quadrupole moment with respect to ab initio as a function of bondangle for water calculated by static and geometry-dependent HF/6-31G* Gaussian quadrupoles.

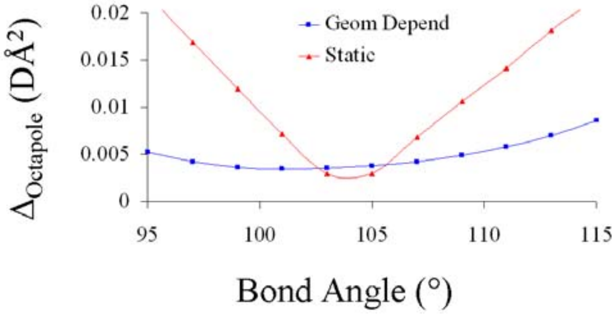

Figure SI.4. Error in molecular octapole moment with respect to ab initio as a function of bondangle for water calculated by static and geometry-dependent HF/6-31G* Gaussian quadrupoles.

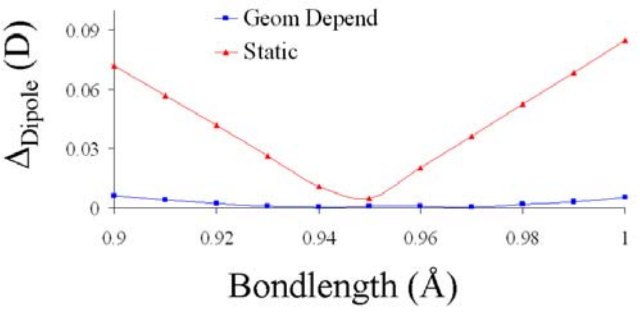

Figure SI.5. Error in molecular dipole moment with respect to ab initio as a function of bondlength for water calculated by static and geometry-dependent HF/6-31G* Gaussian dipoles.

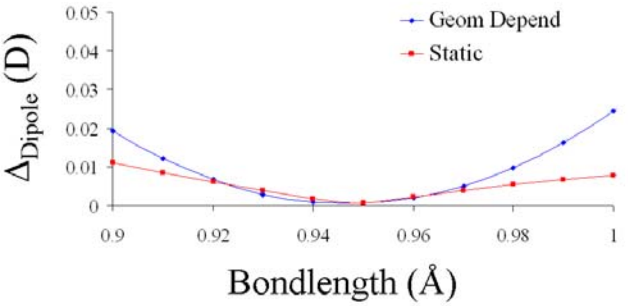

Figure SI.6. Error in molecular dipole moment with respect to ab initio as a function of bondlength for water calculated by static and geometry-dependent HF/6-31G* Gaussian quadrupoles.

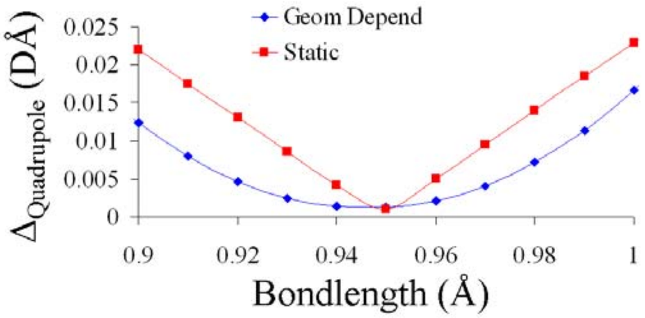

Figure SI.7. Error in molecular quadrupole moment with respect to ab initio as a function of bondlength for water calculated by static and geometry-dependent HF/6-31G* Gaussian quadrupoles.

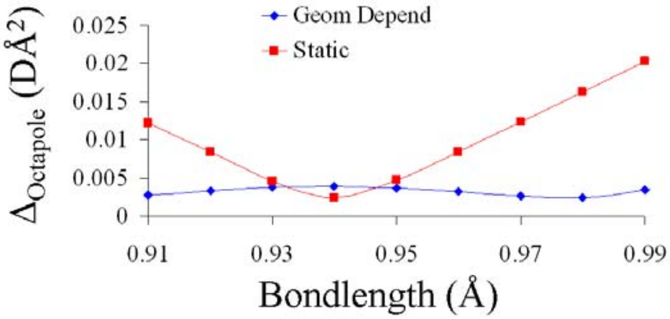

Figure SI.8. Error in molecular octapole moment with respect to ab initio as a function of bondlength for water calculated by static and geometry-dependent HF/6-31G* Gaussian quadrupoles.