

## Supplementary Information

### **Large-scale compensation of errors in pairwise-additive empirical force fields: comparison of AMBER intermolecular terms with rigorous DFT-SAPT calculations.**

Marie Zgarbová<sup>1</sup>, Michal Otyepka<sup>1</sup>, Jiří Šponer<sup>1,2</sup>, Pavel Hobza<sup>1,3</sup>, and Petr Jurečka\*<sup>1,2</sup>

<sup>1</sup>*Department of Physical Chemistry, Palacký University, tř. 17. listopadu 12, 771 46 Olomouc, Czech Republic*

<sup>2</sup>*Institute of Biophysics, Academy of Sciences of the Czech Republic, Královopolská 135, 612 65 Brno, Czech Republic*

<sup>3</sup>*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center of Biomolecules and Complex Molecular Systems, Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic*

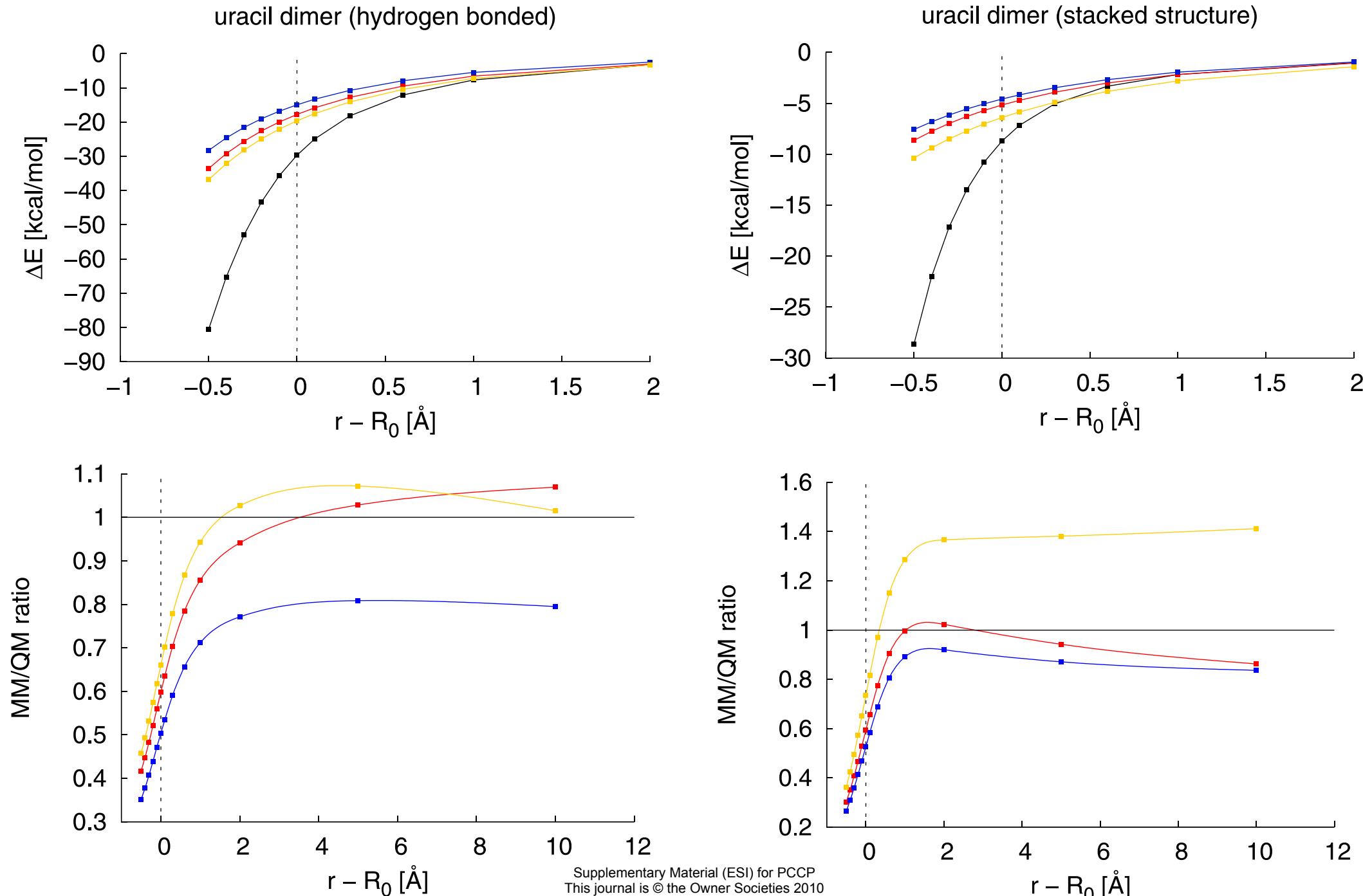
\* Corresponding Author

Petr Jurečka: petr.jurecka@upol.cz

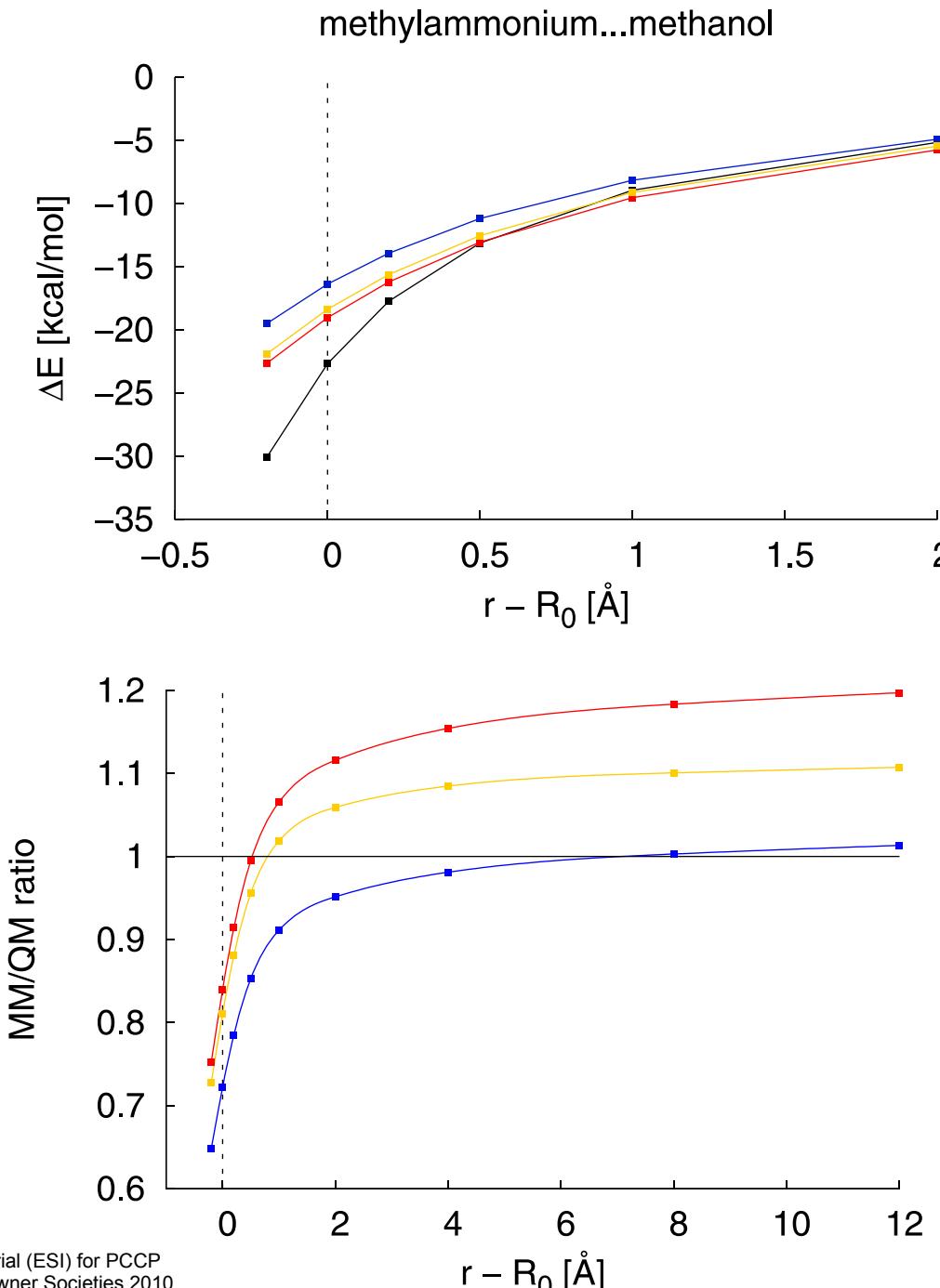
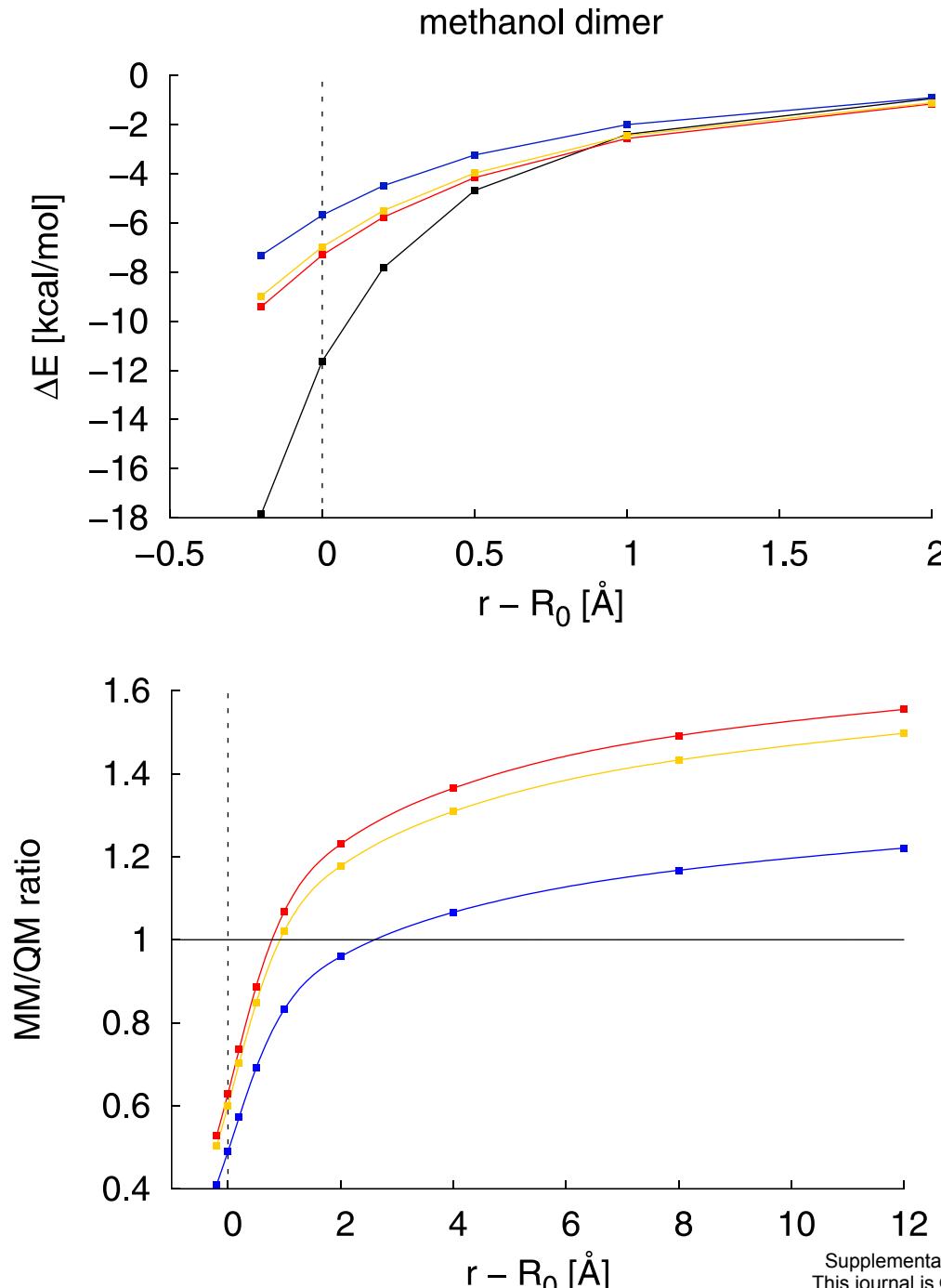
#### Contents:

1. Plots of all components of the interaction energy	2-22
2. Plots of absolute errors of the individual interaction energy components	23-26
3. Tables of the interaction energy	27-32

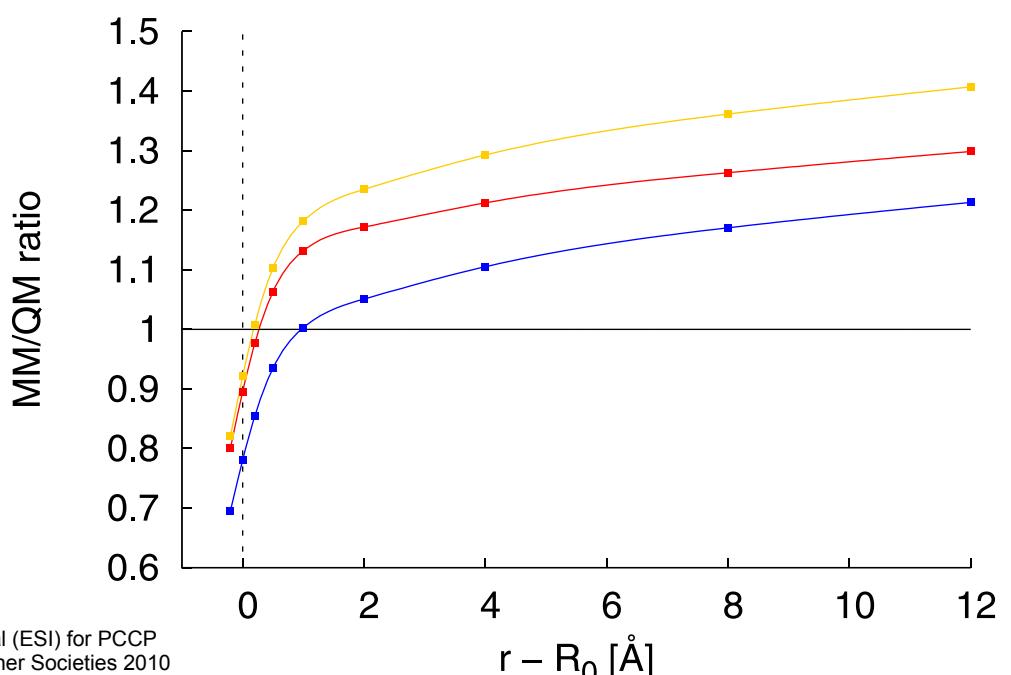
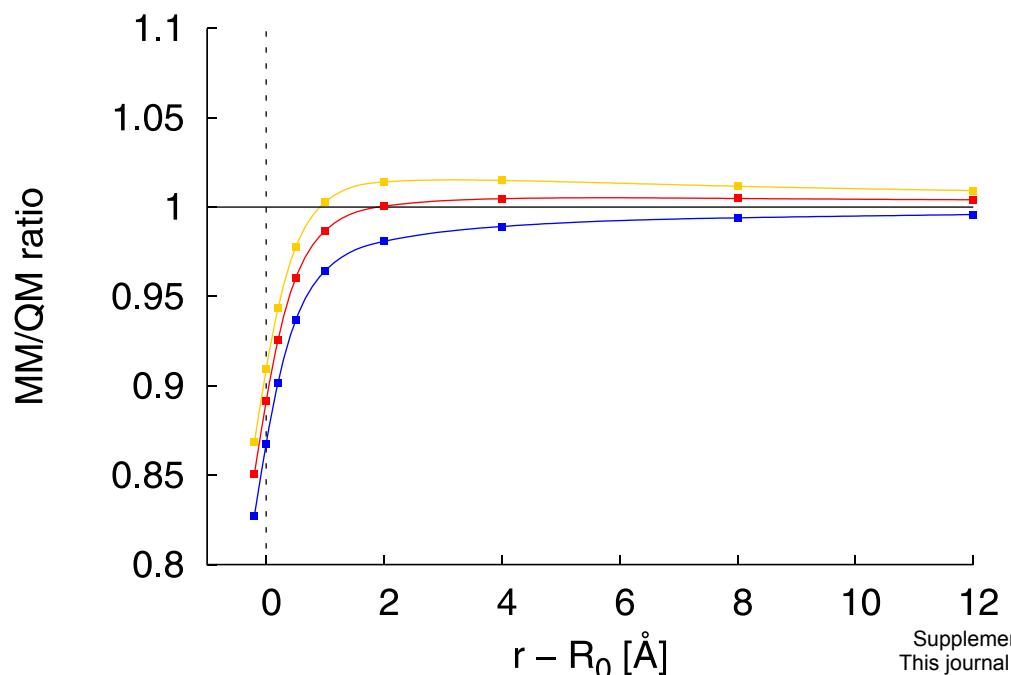
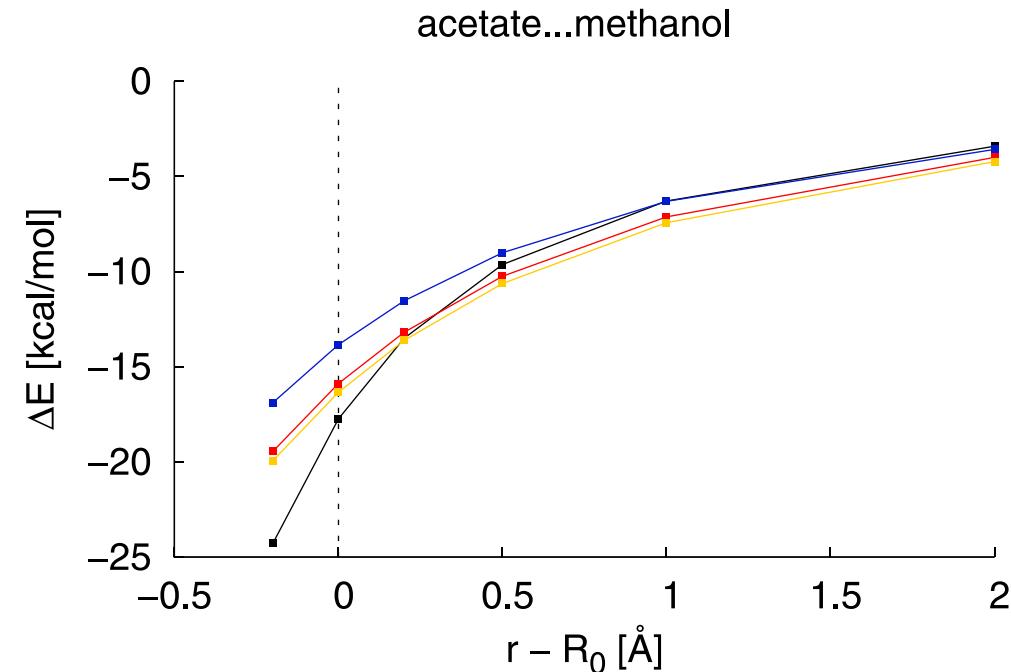
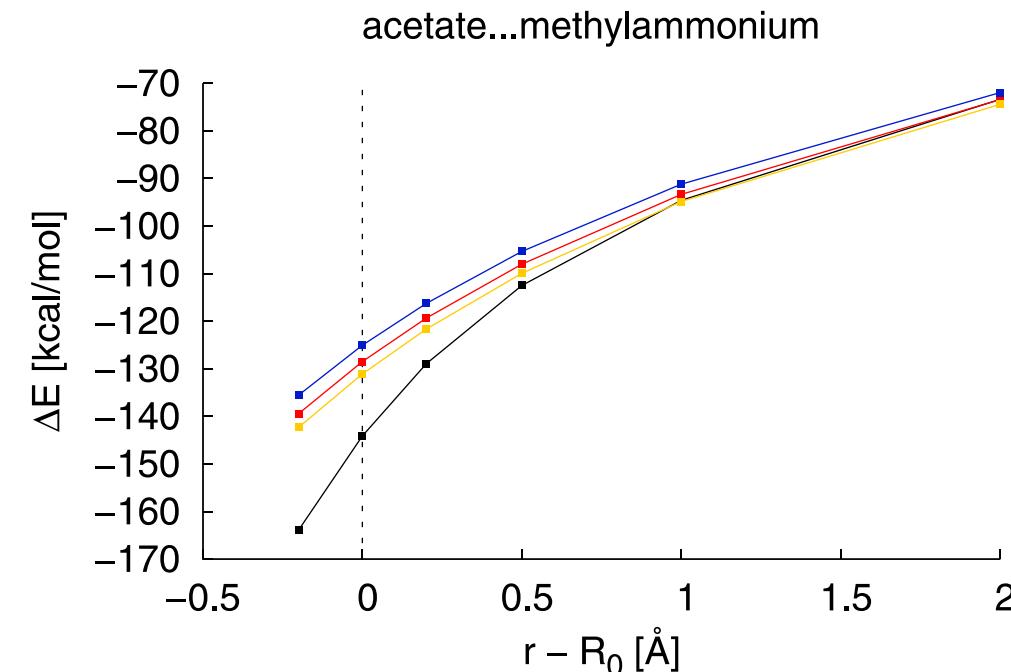
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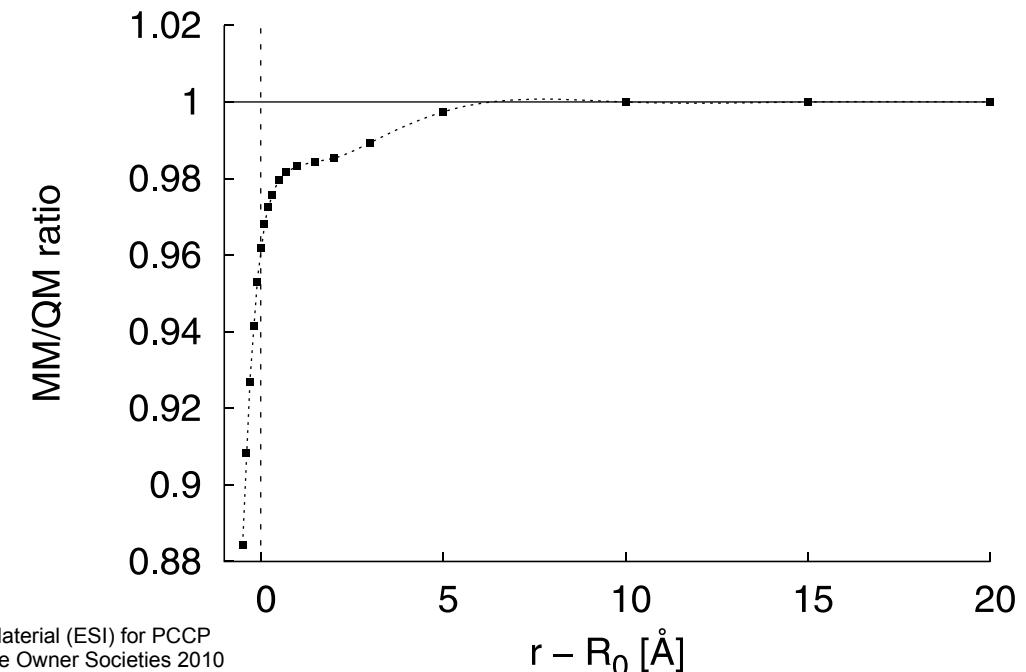
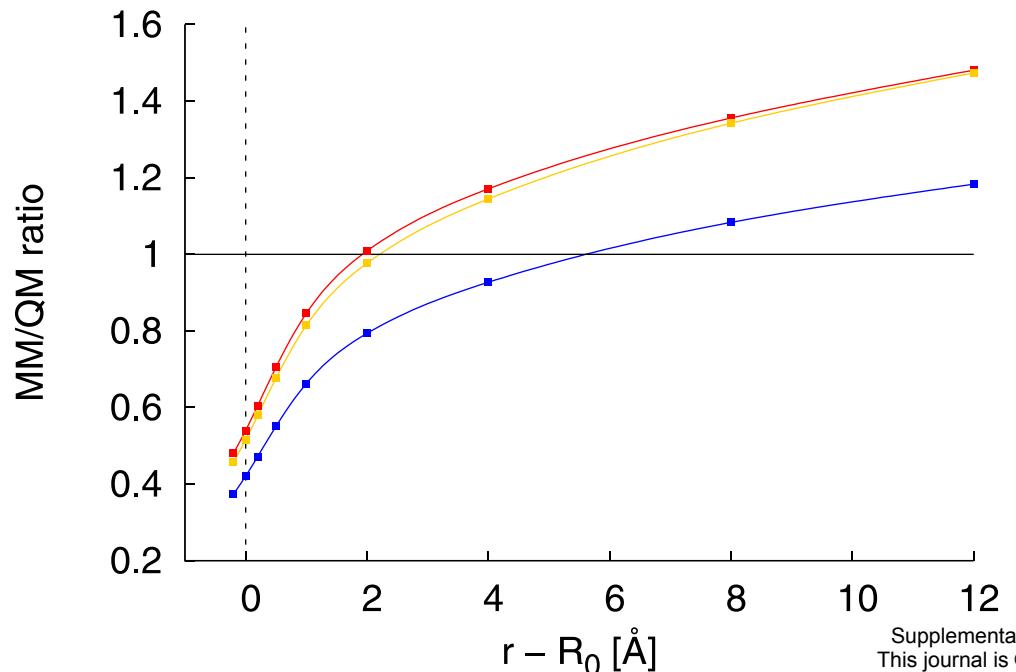
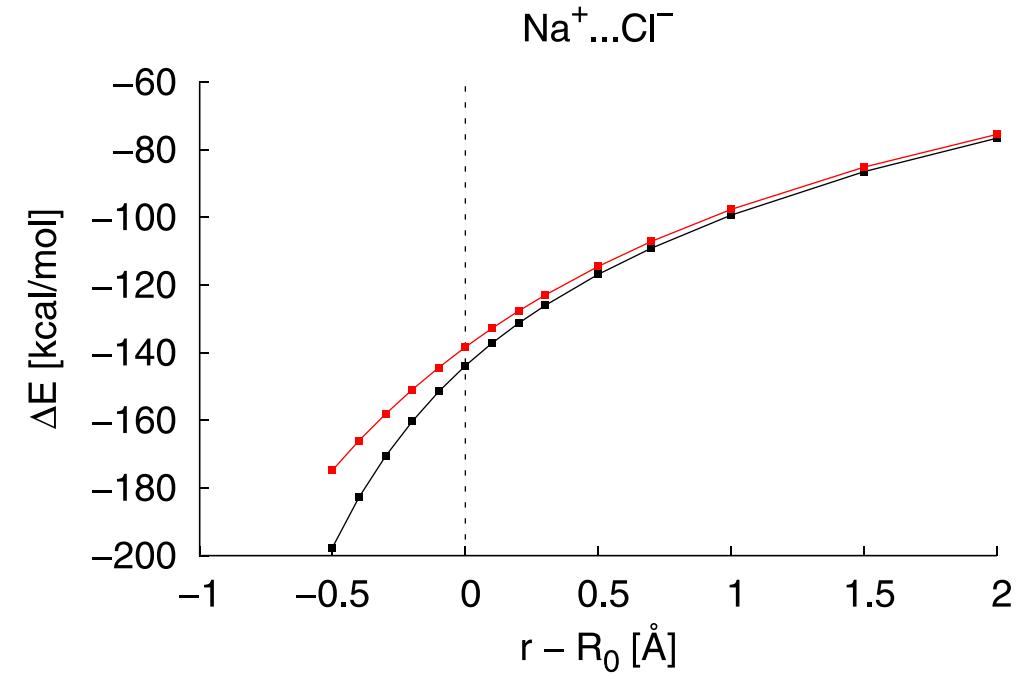
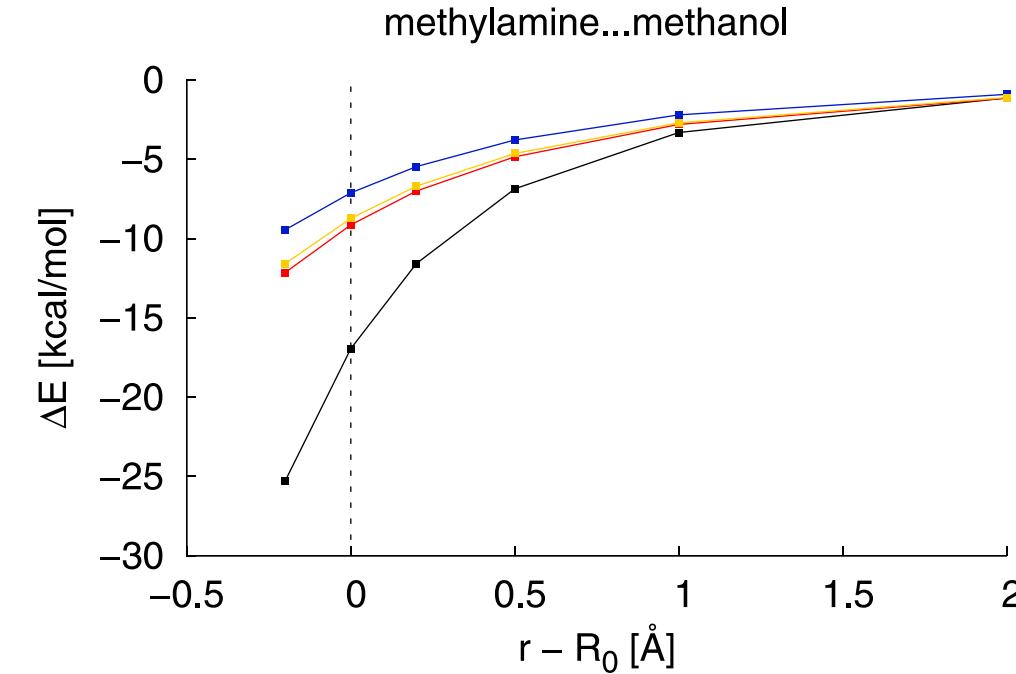
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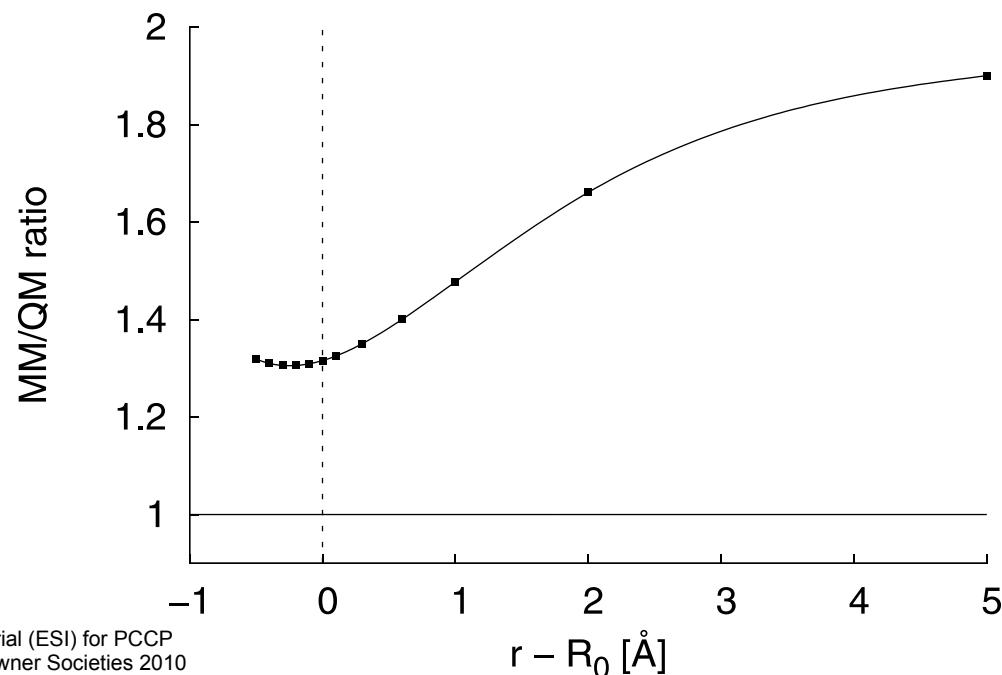
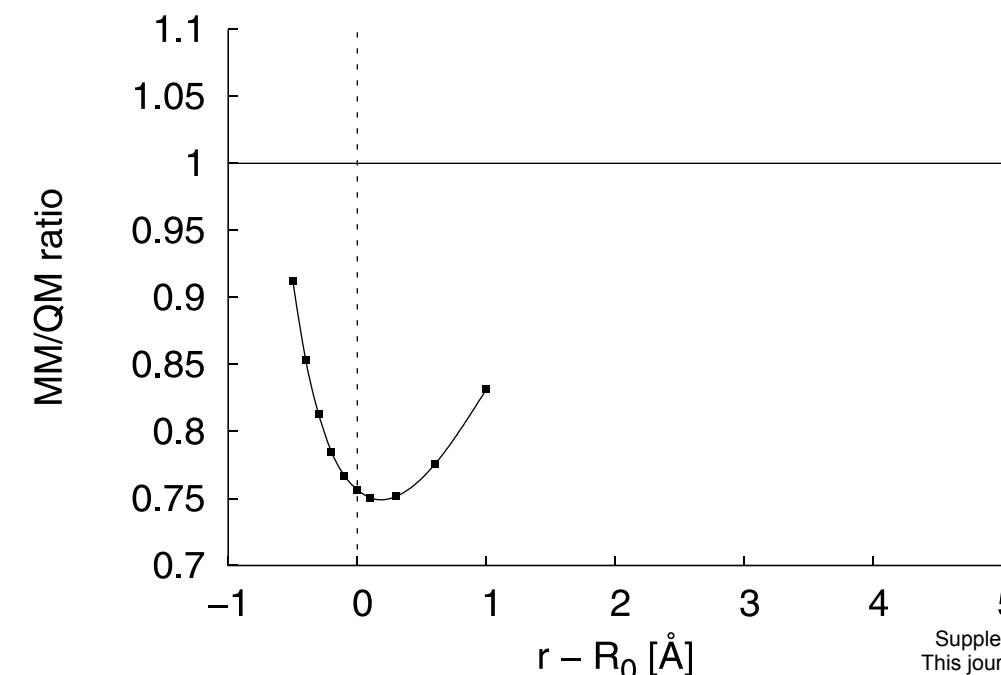
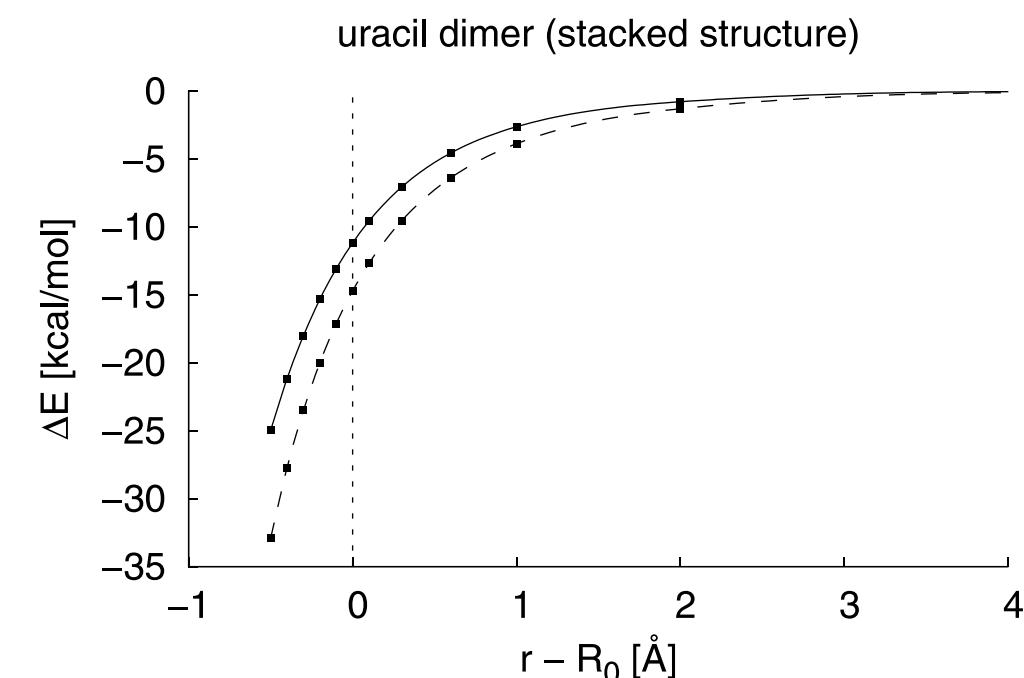
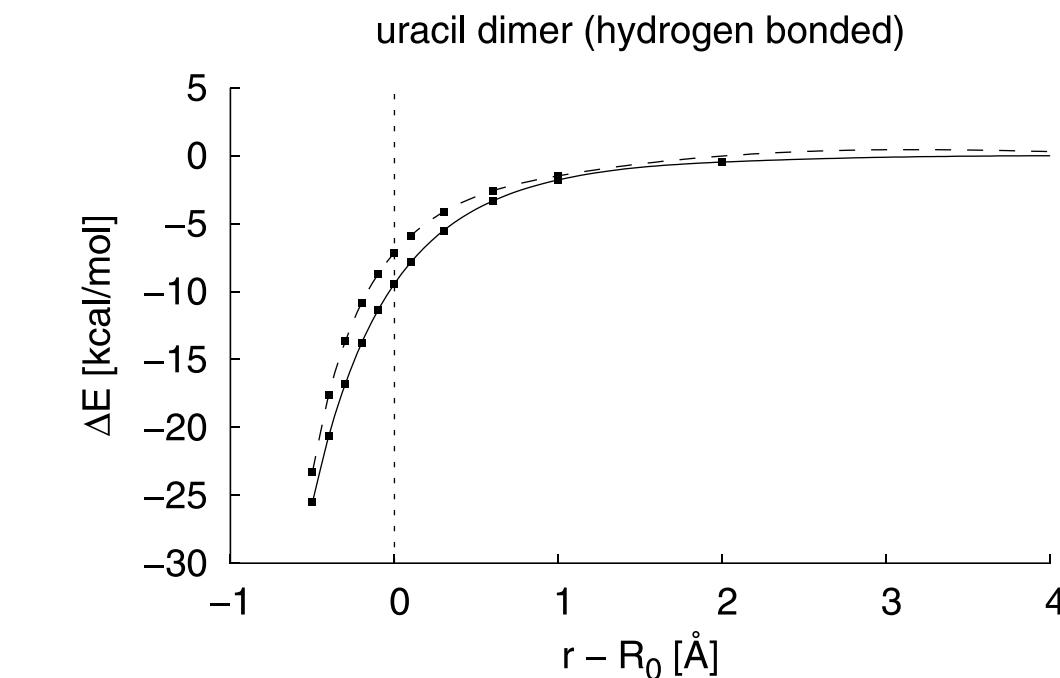
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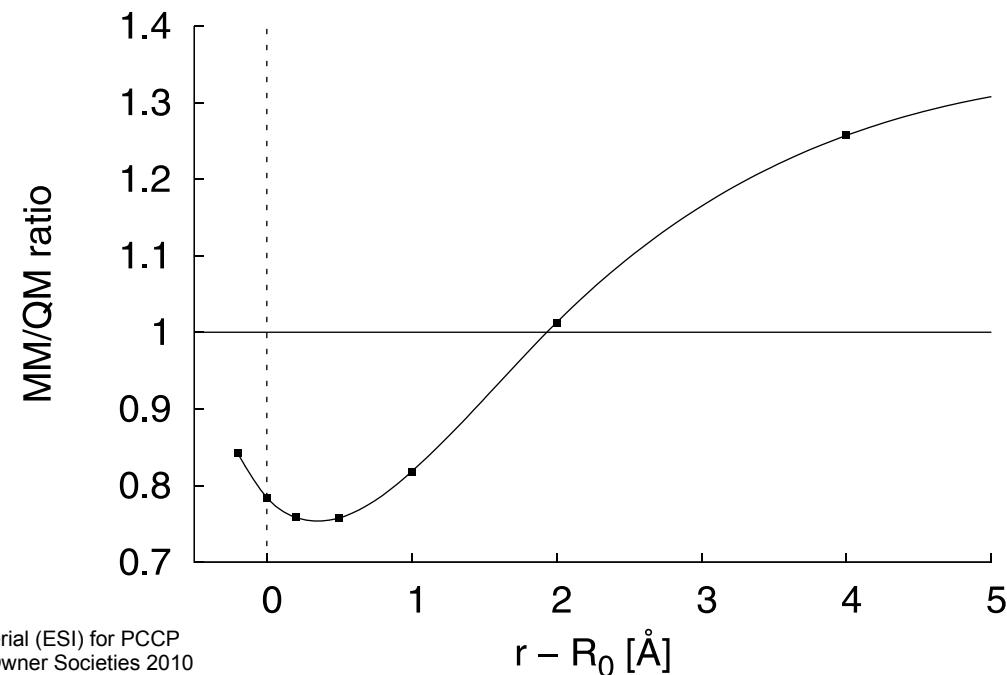
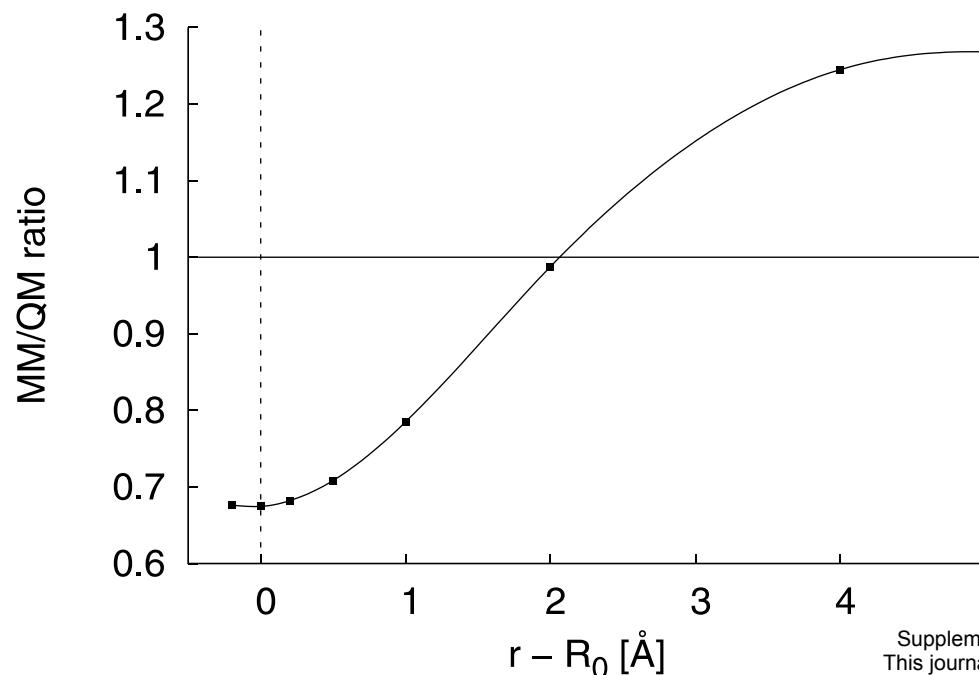
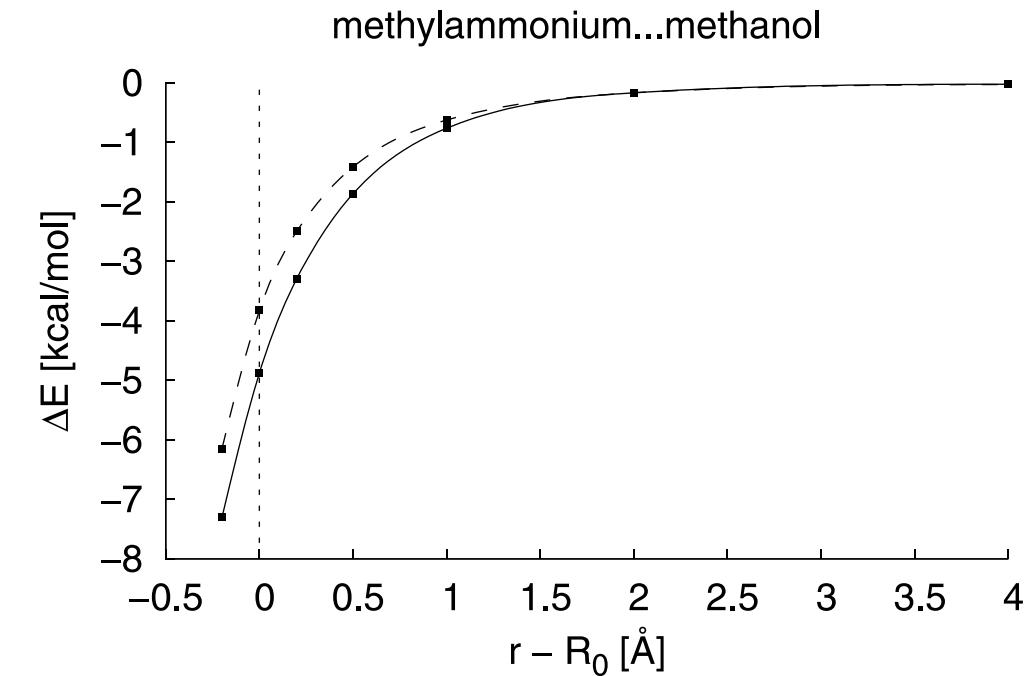
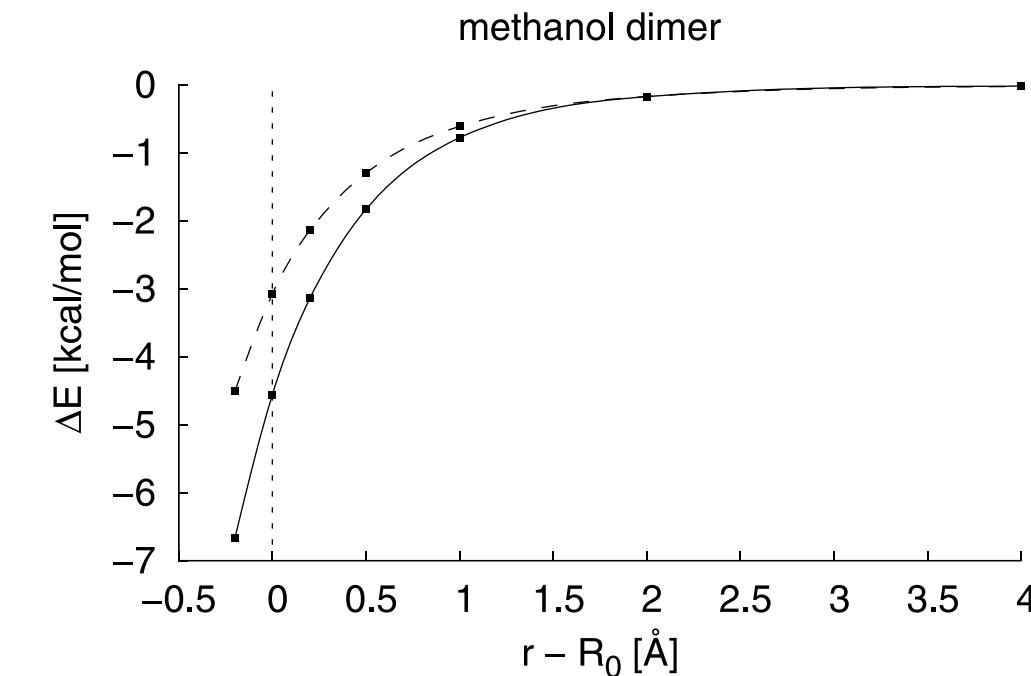
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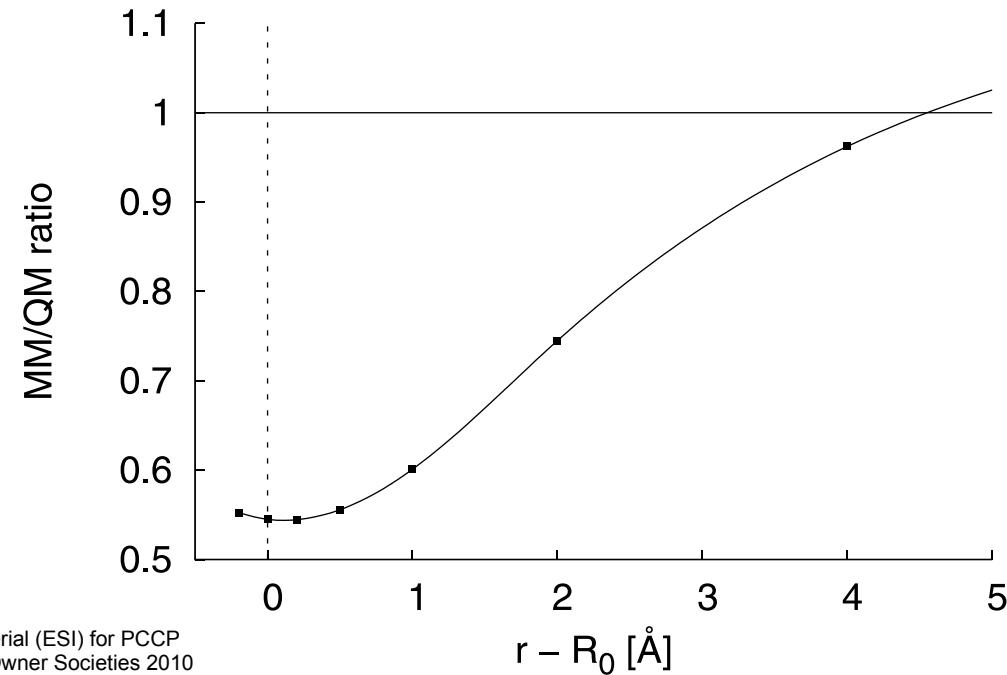
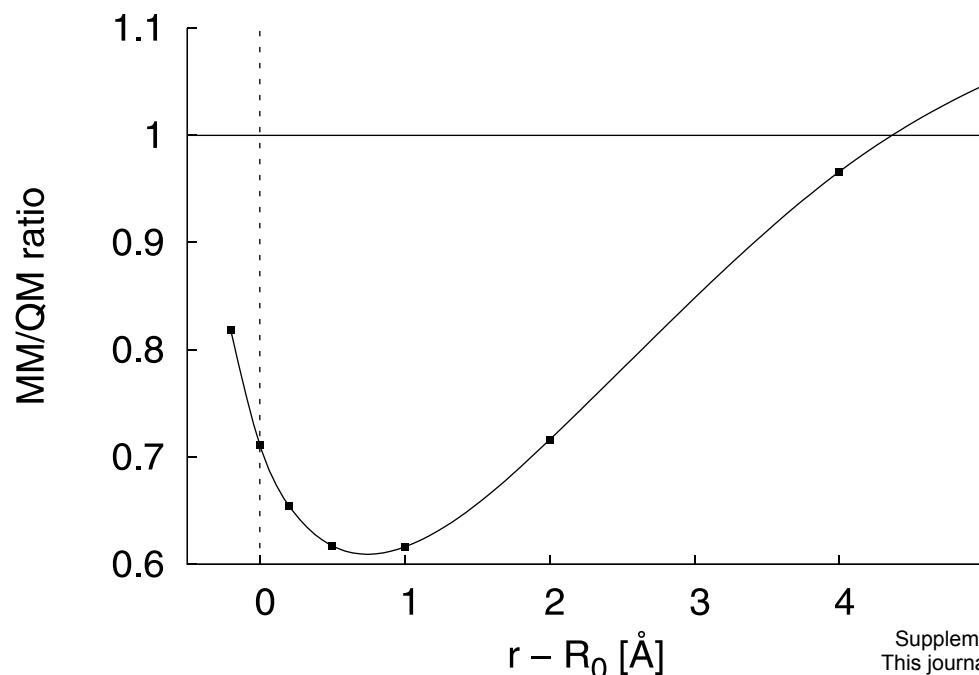
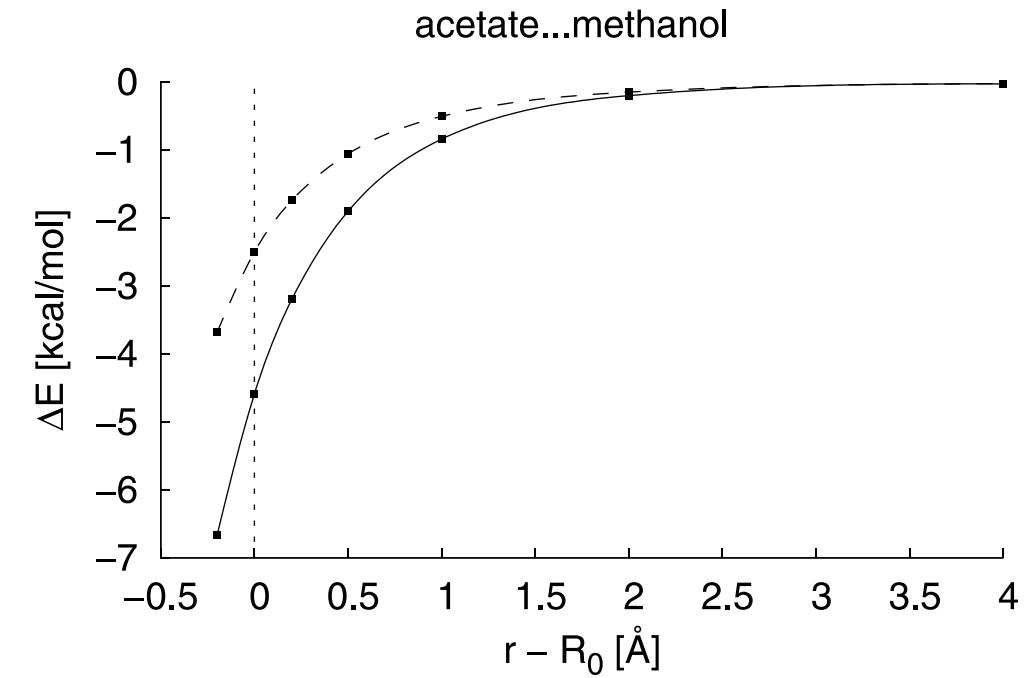
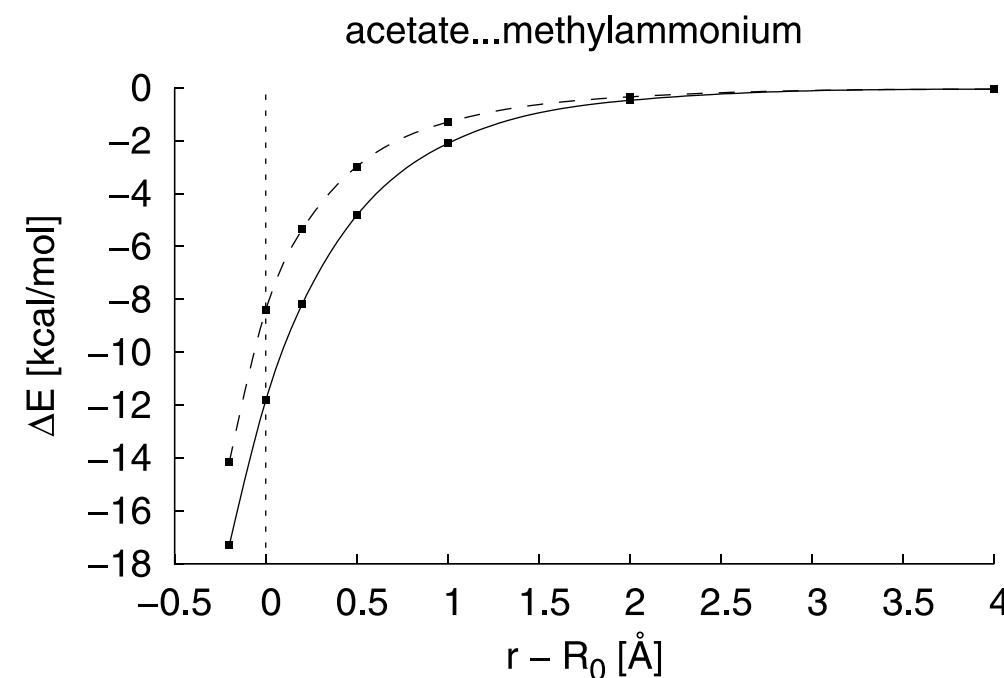
**Figure S2.** Dispersion component of force field interaction energies (MM, dashed line) compared with DFT-SAPT (QM, full line) reference values (top) and the MM/QM ratio (bottom). Zero on the  $x$  axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol.



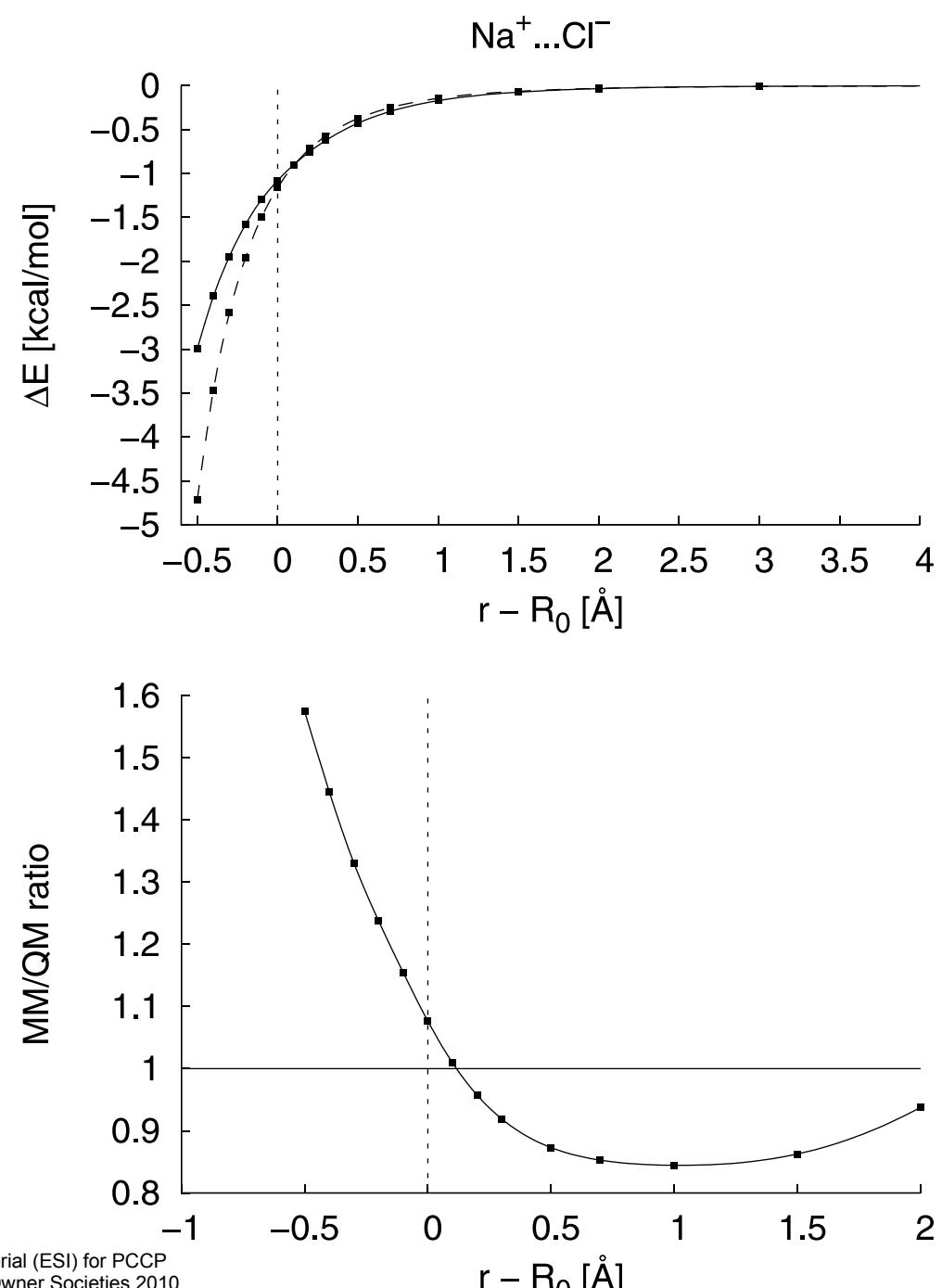
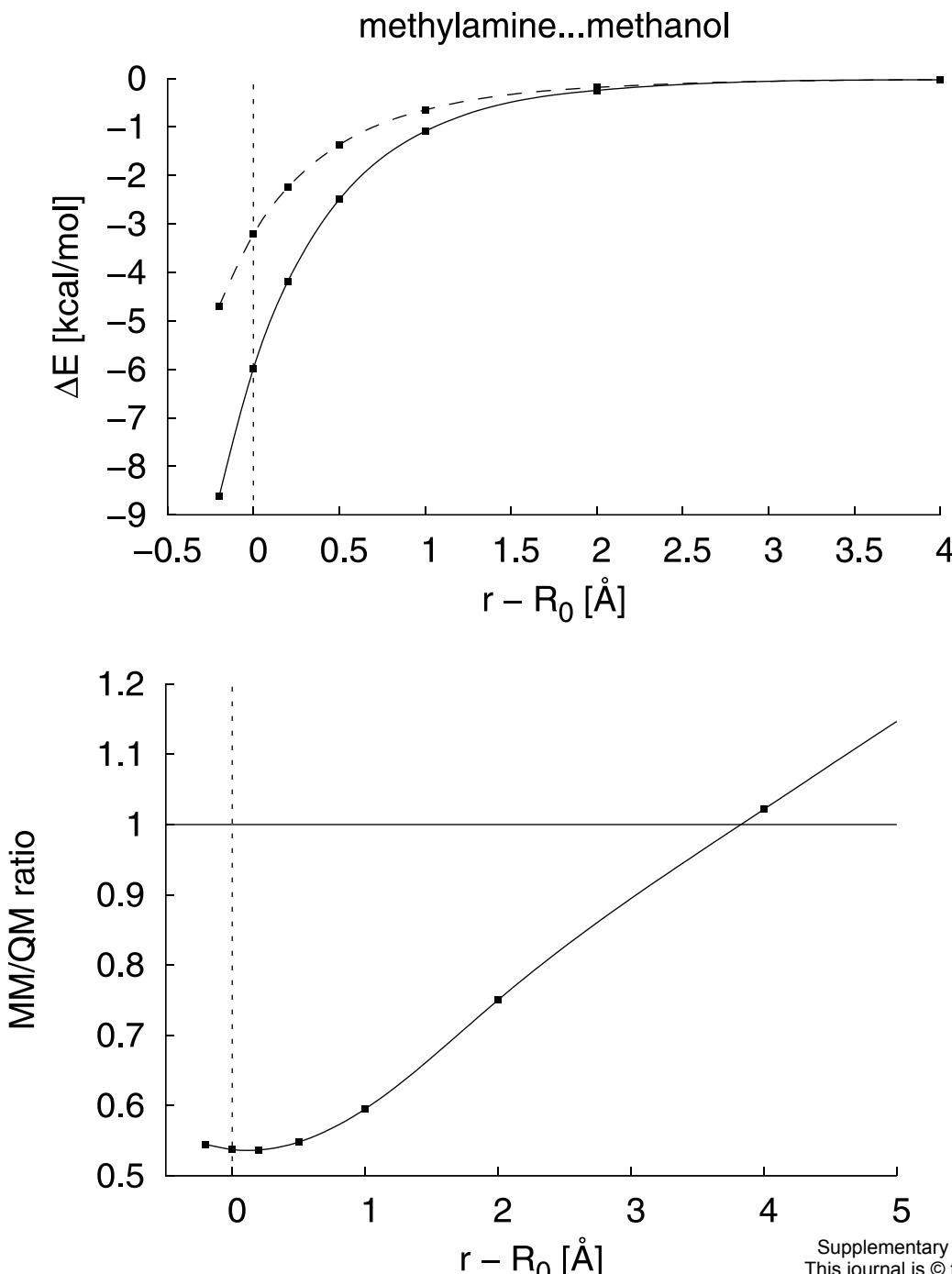
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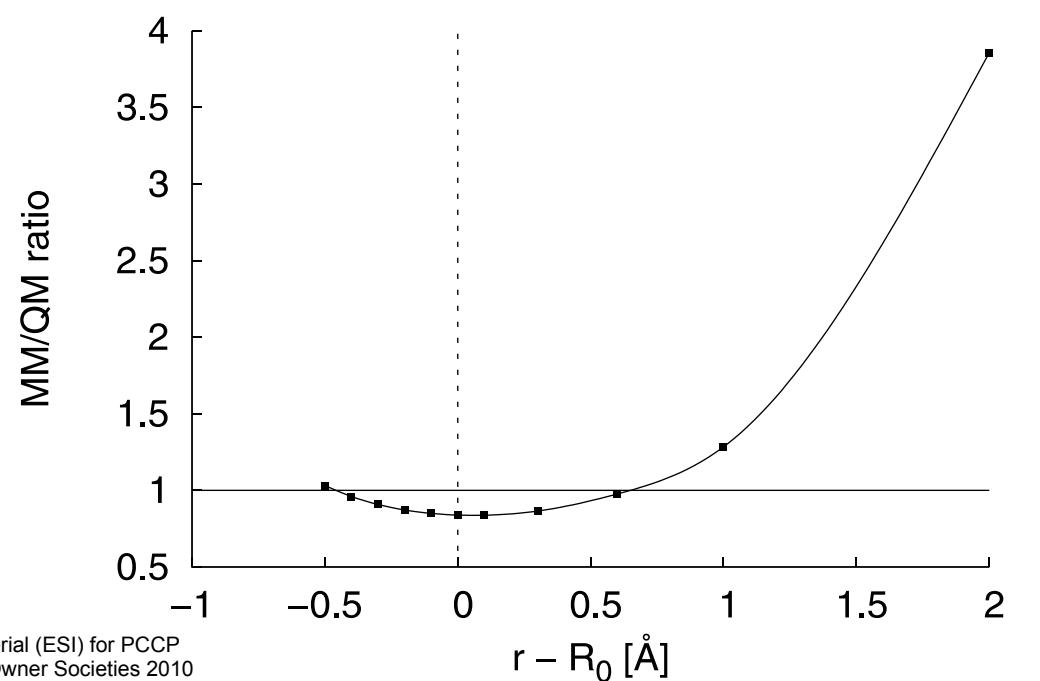
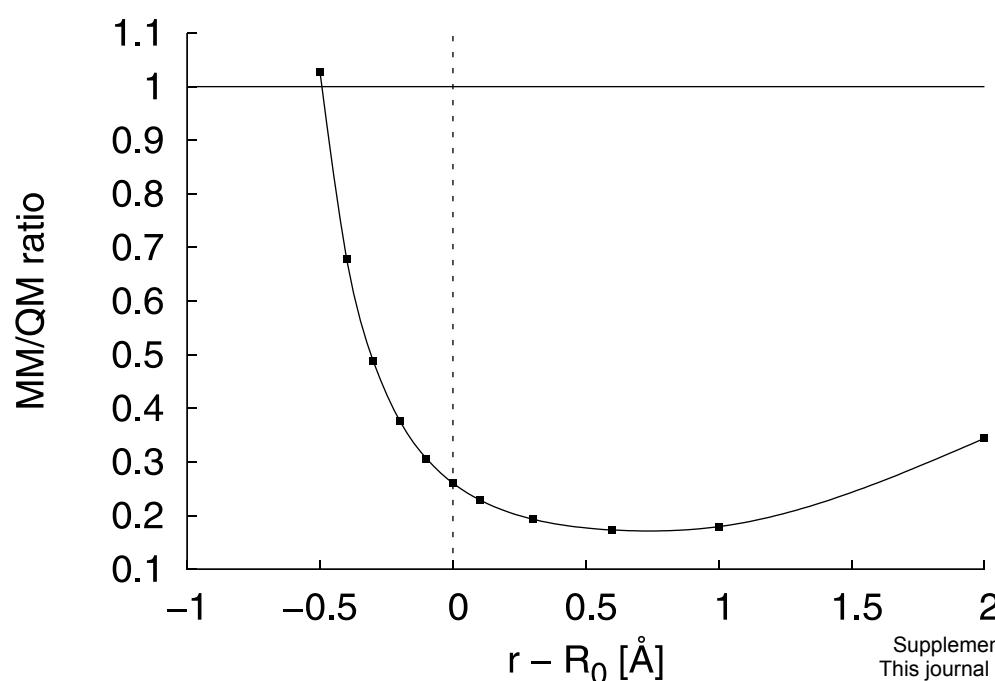
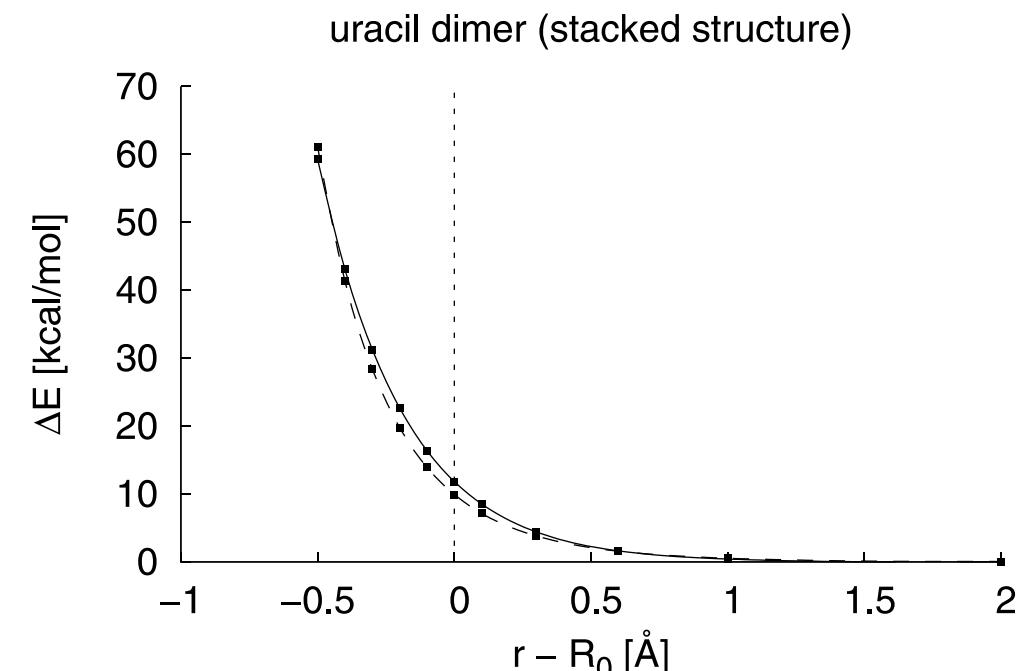
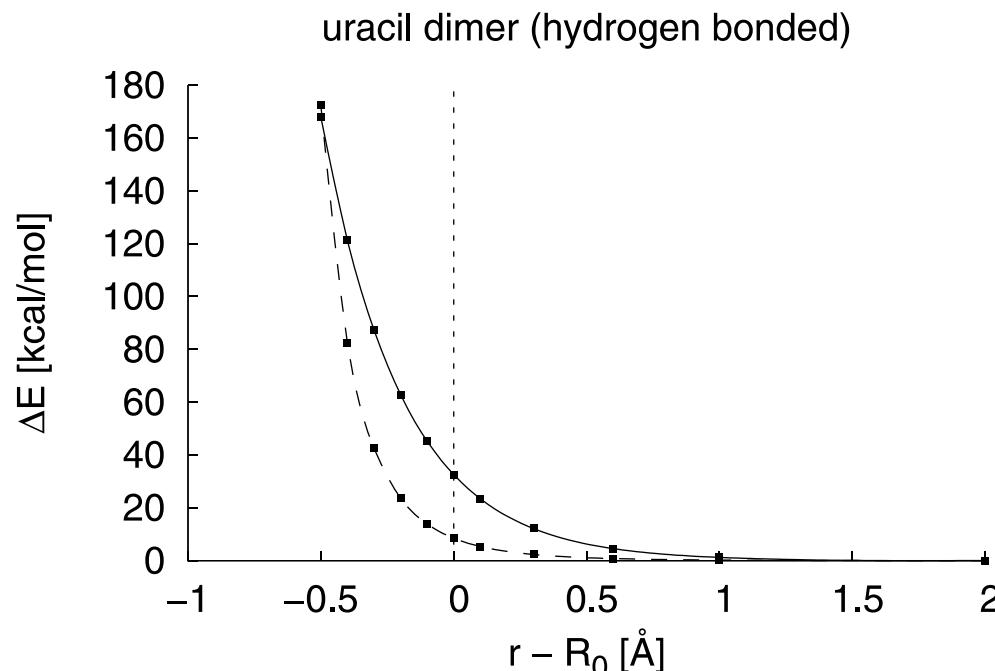
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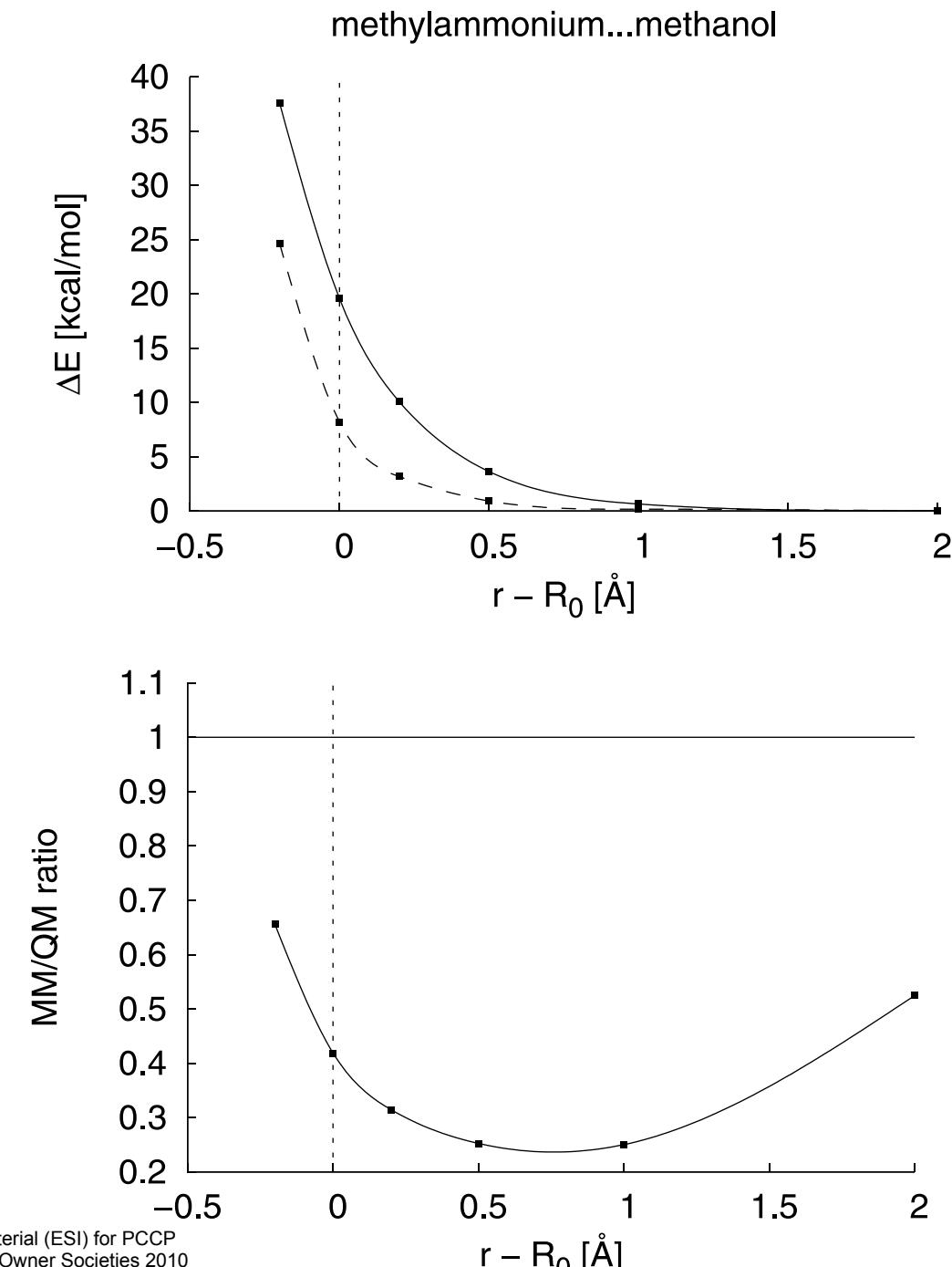
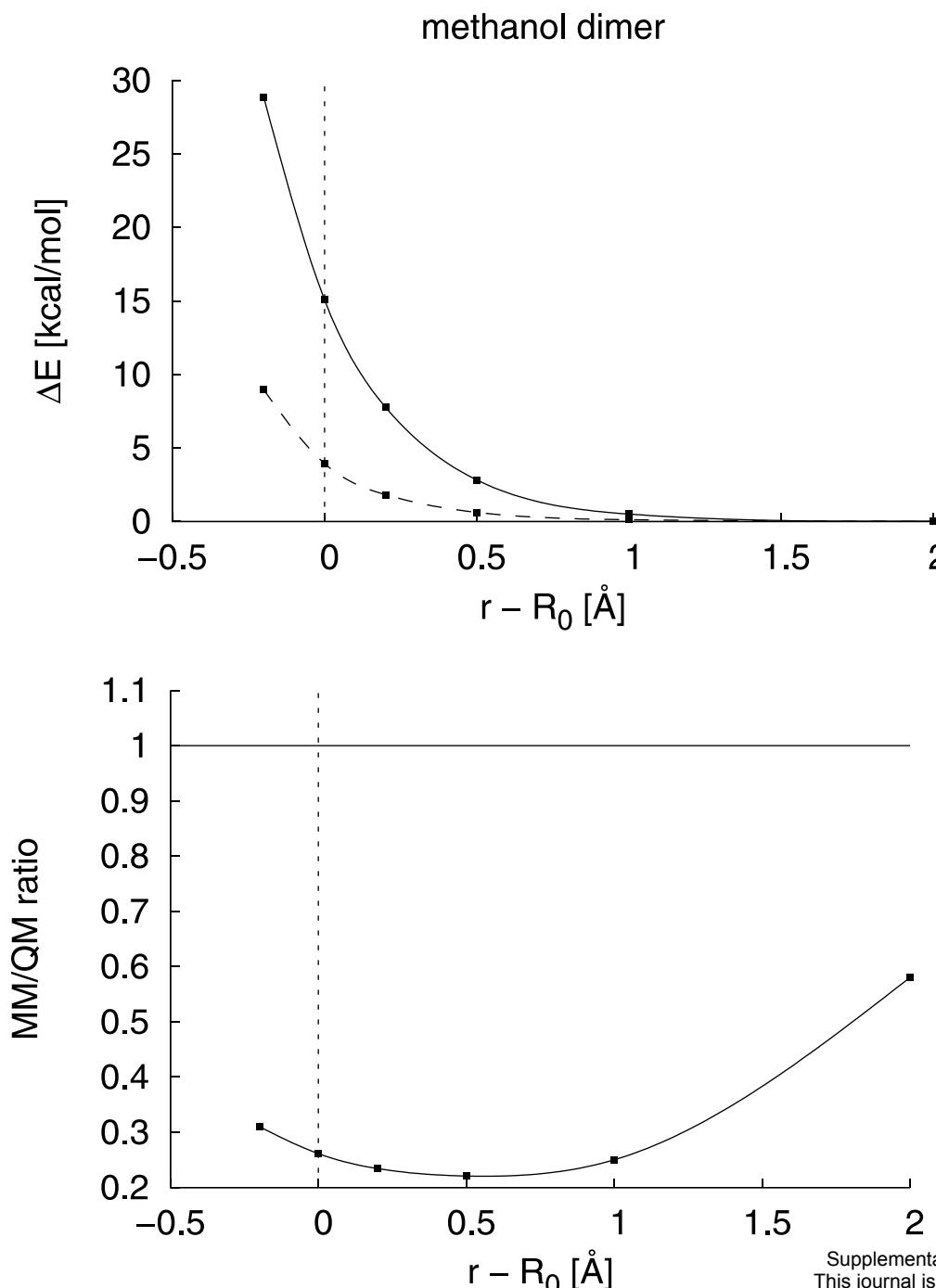
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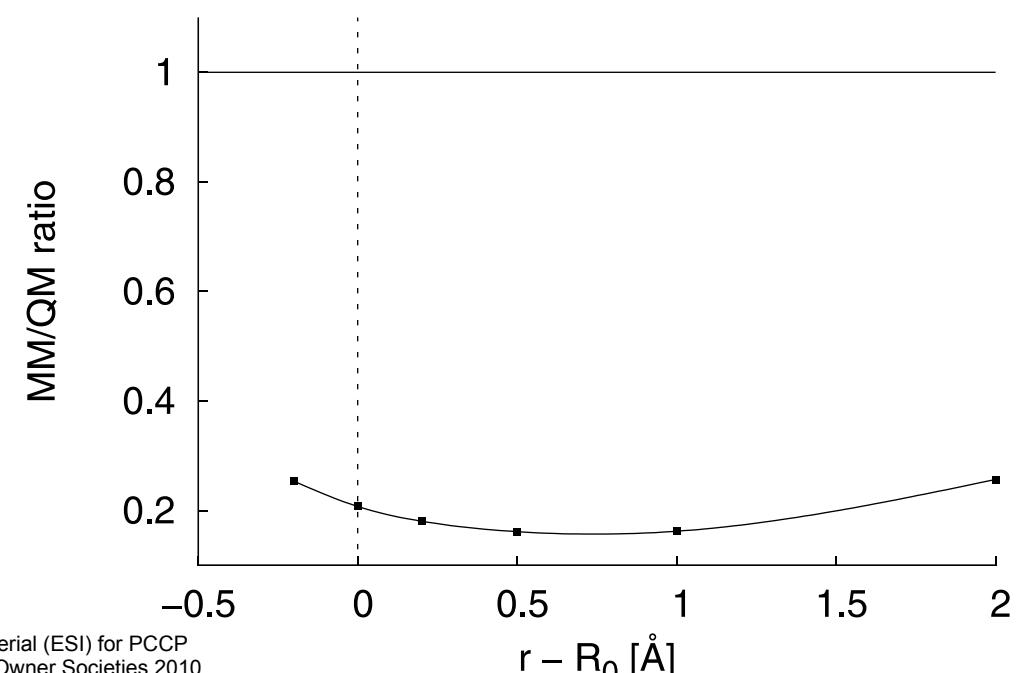
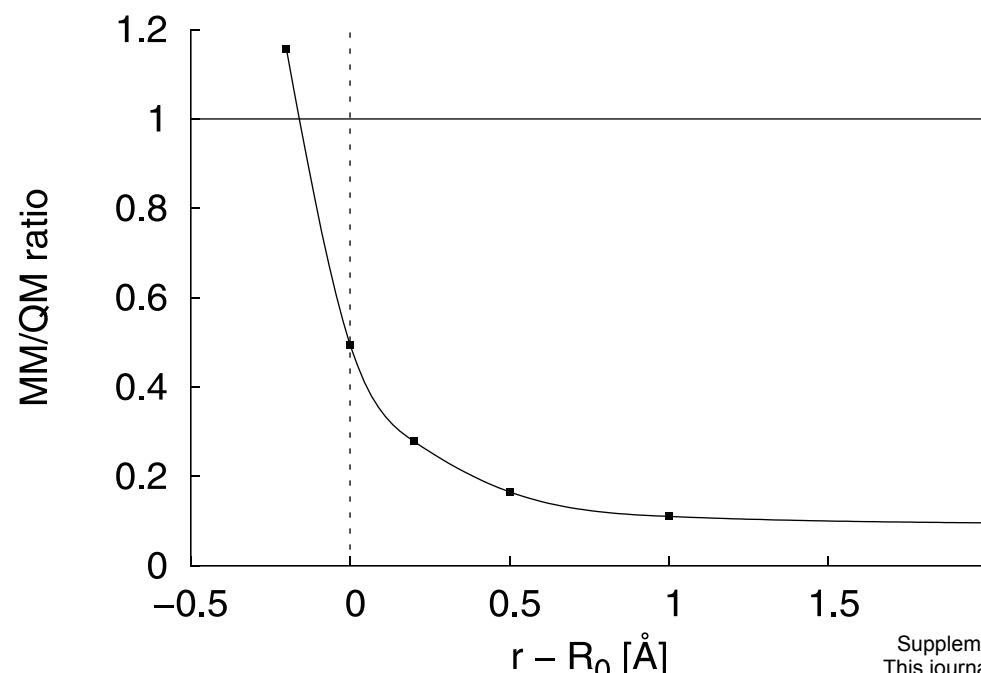
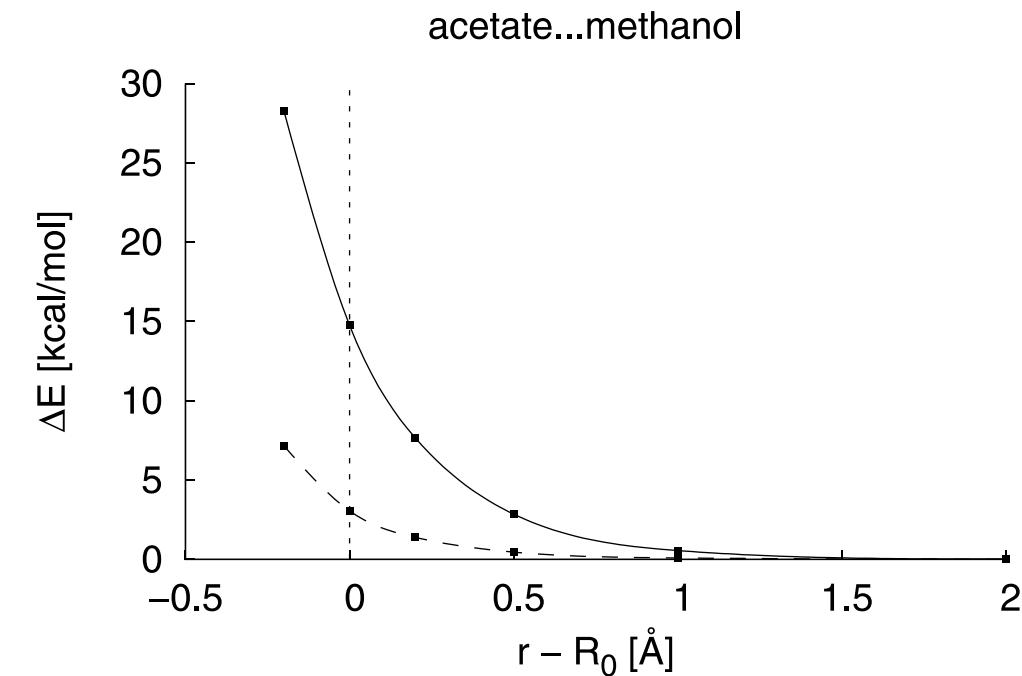
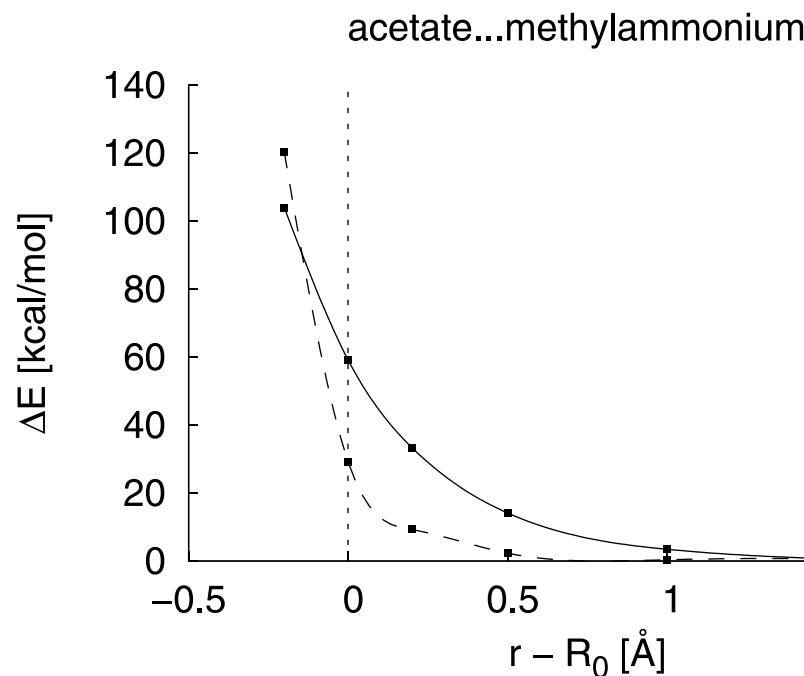
**Figure S3.** Repulsion component of force field interaction energies (MM, dashed line) compared with DFT-SAPT (QM, full line) reference values (top) and the MM/QM ratio (bottom). Zero on the x axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol.



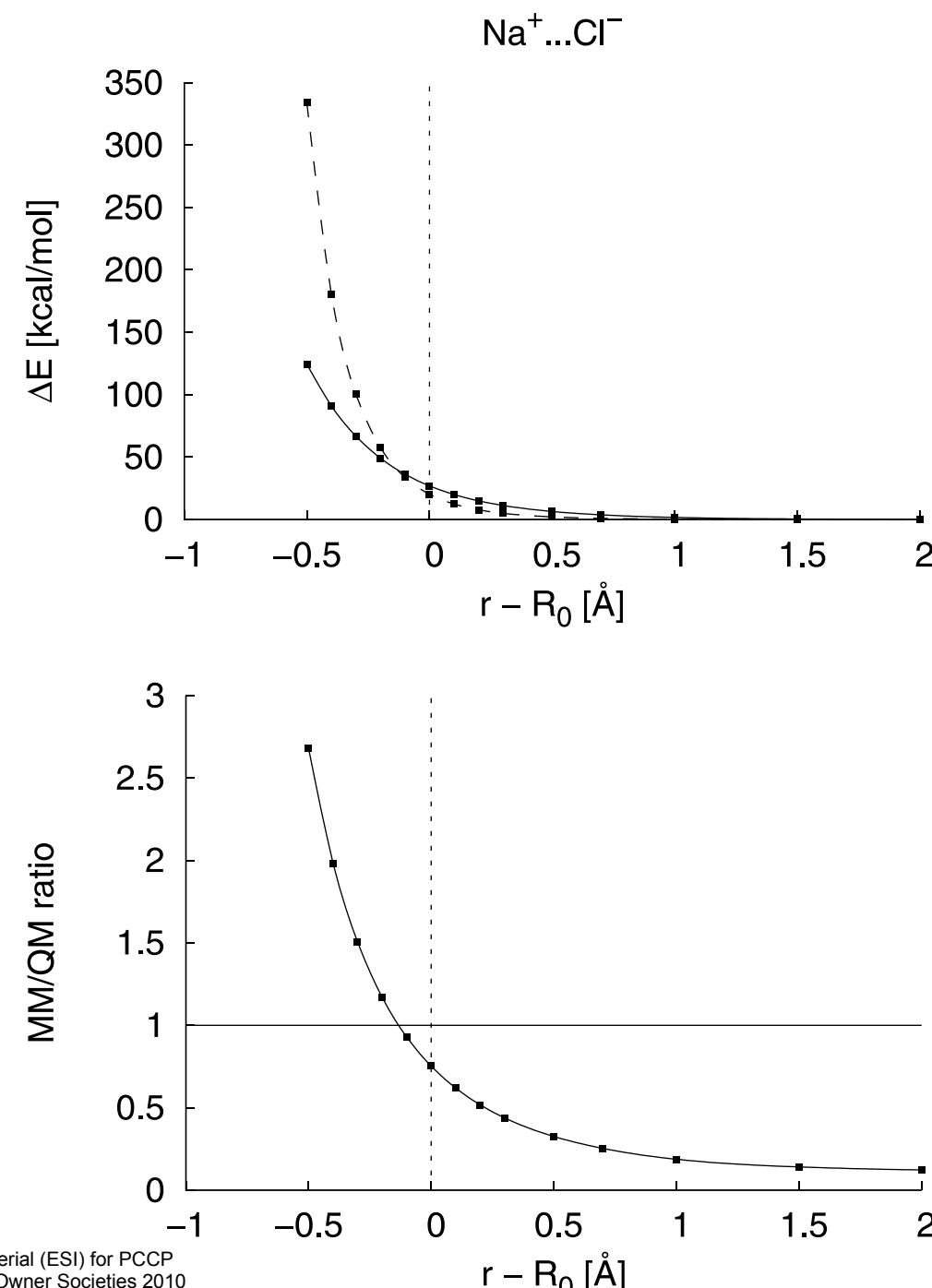
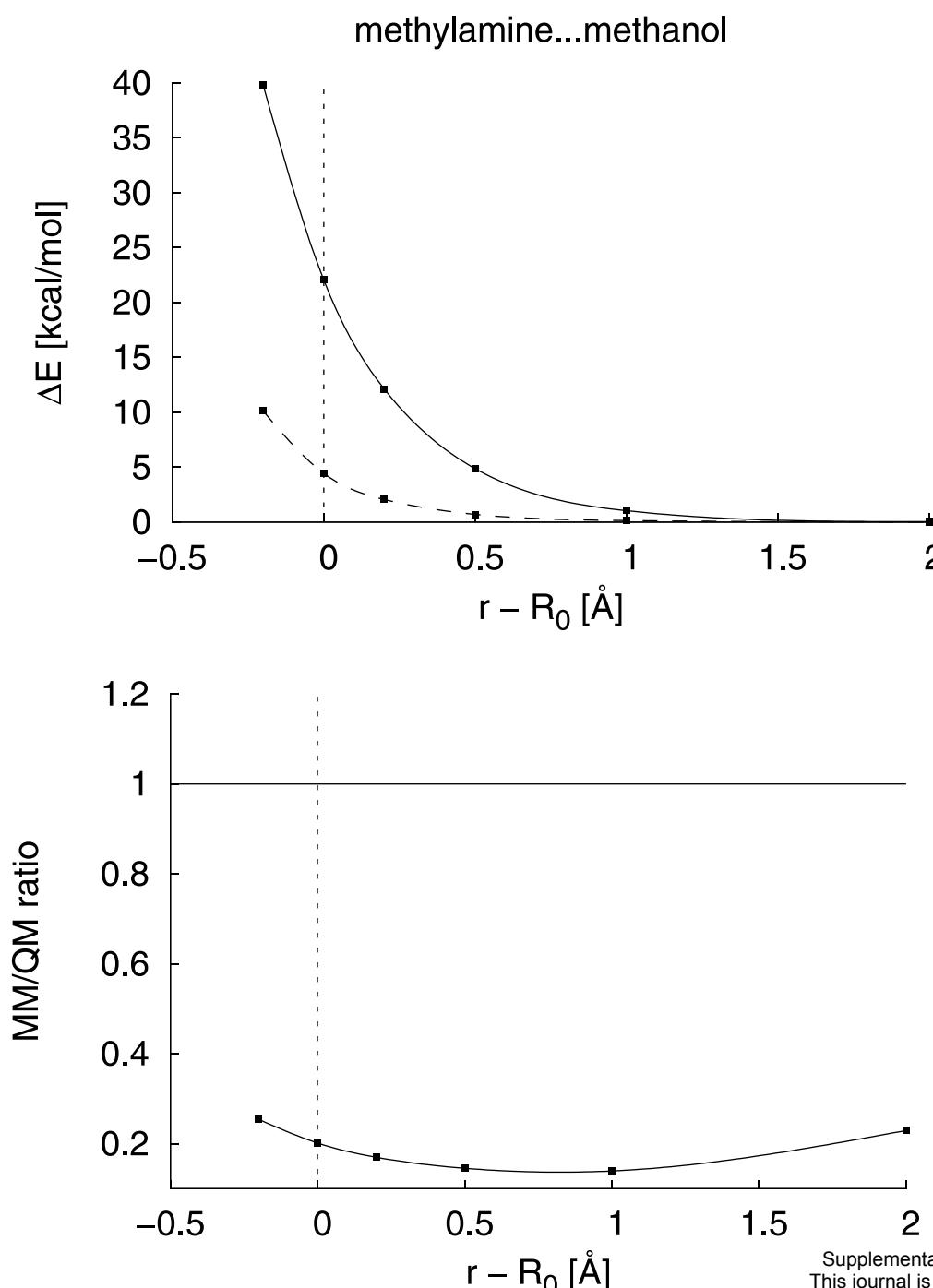
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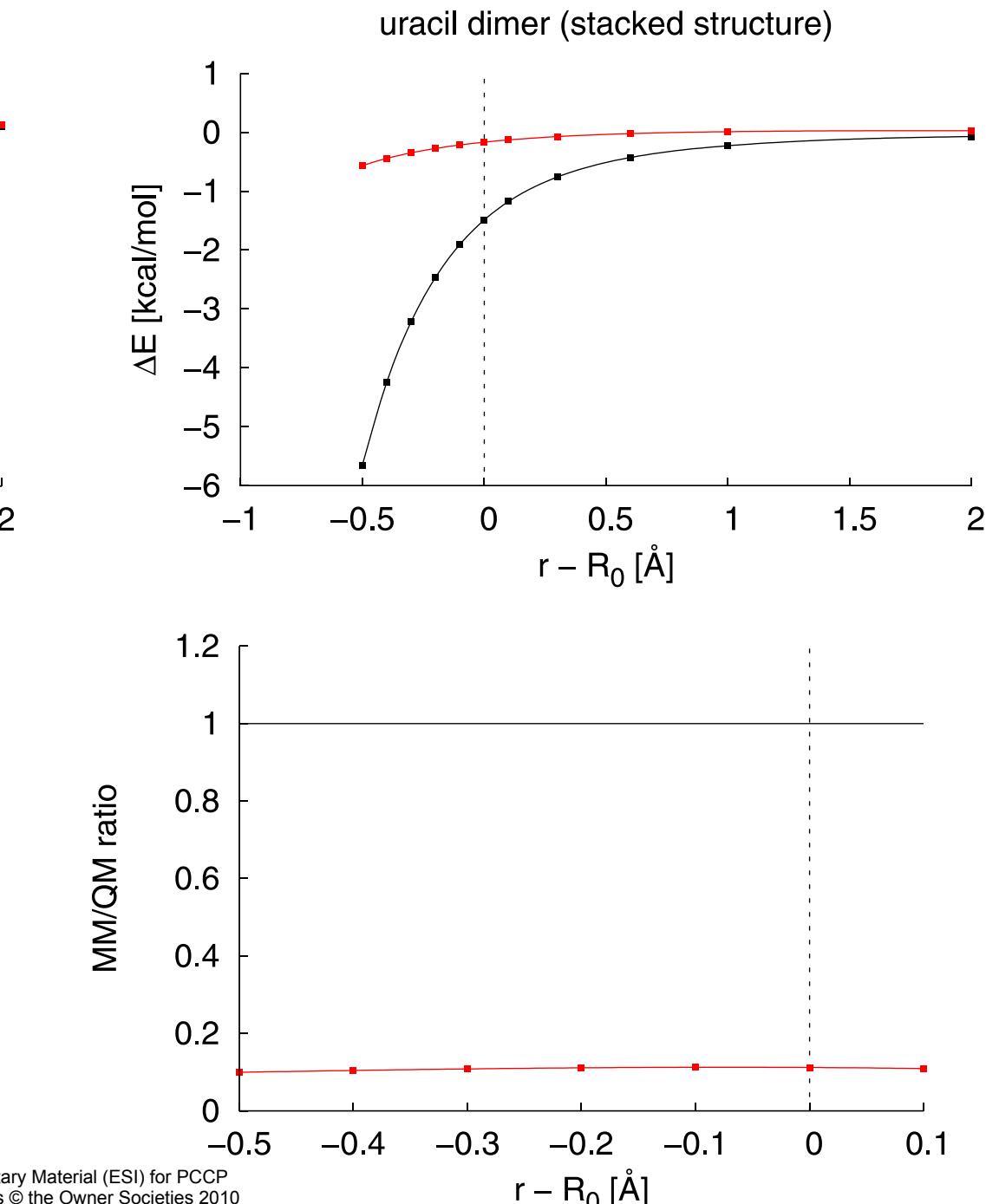
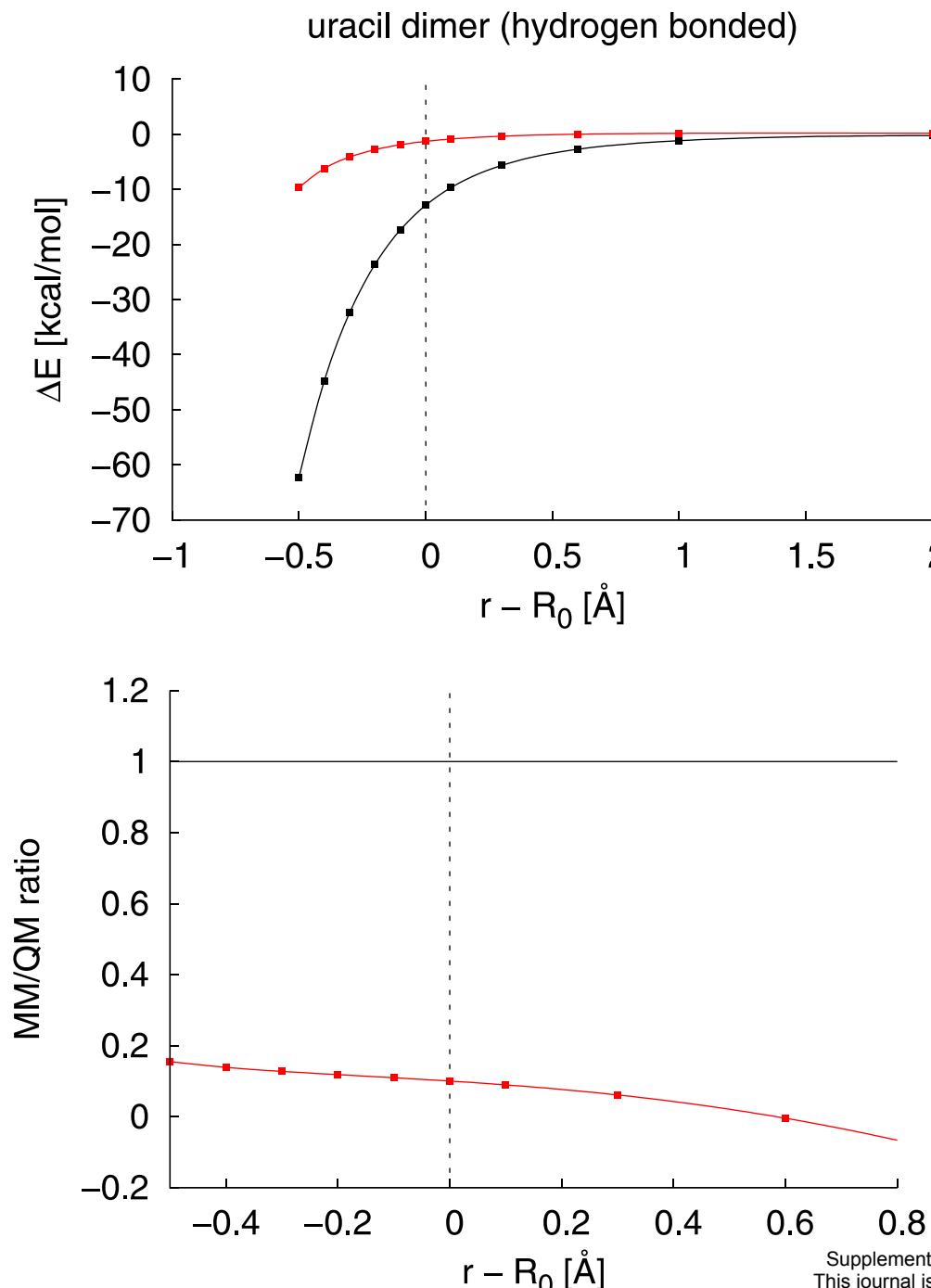
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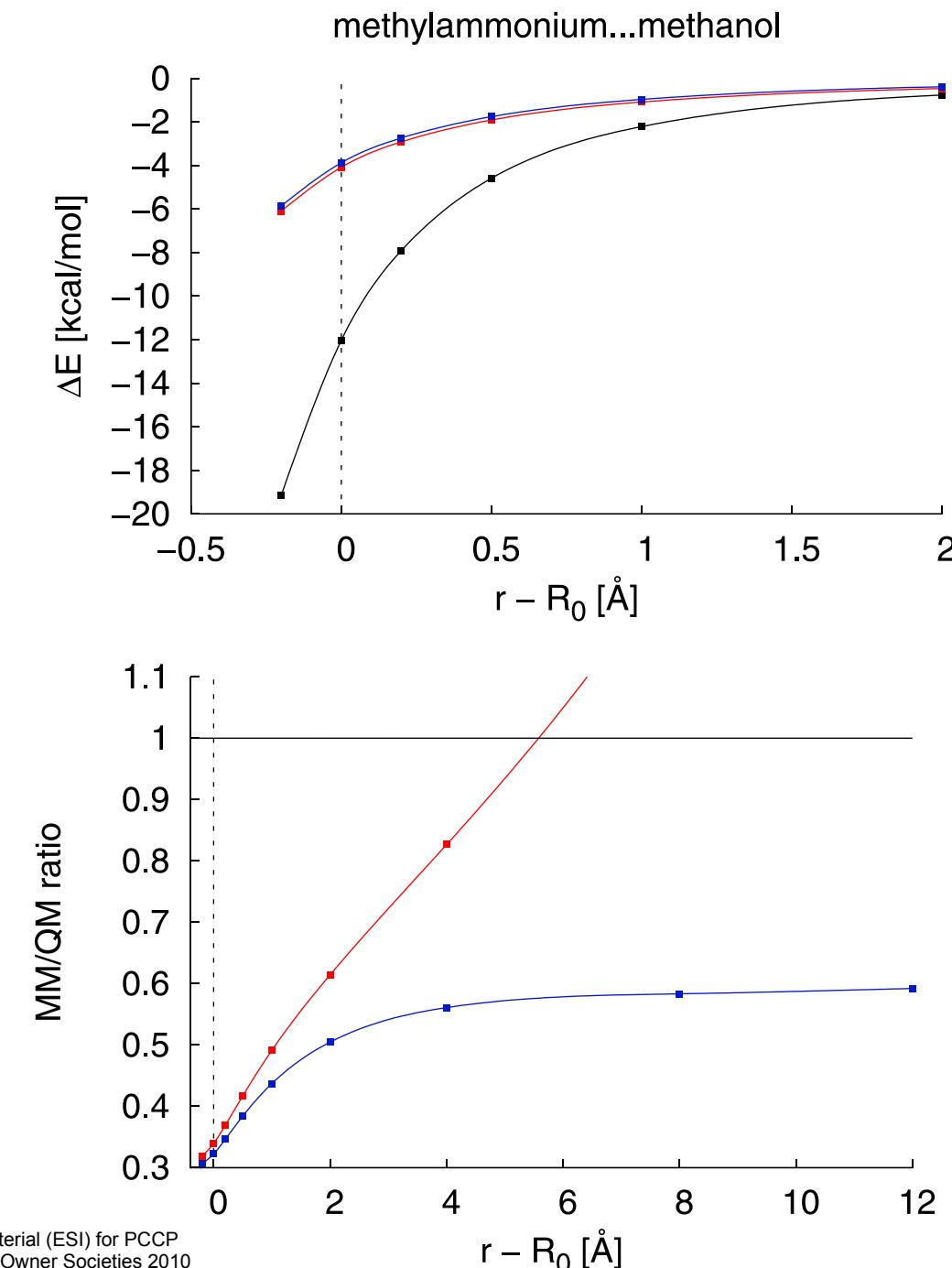
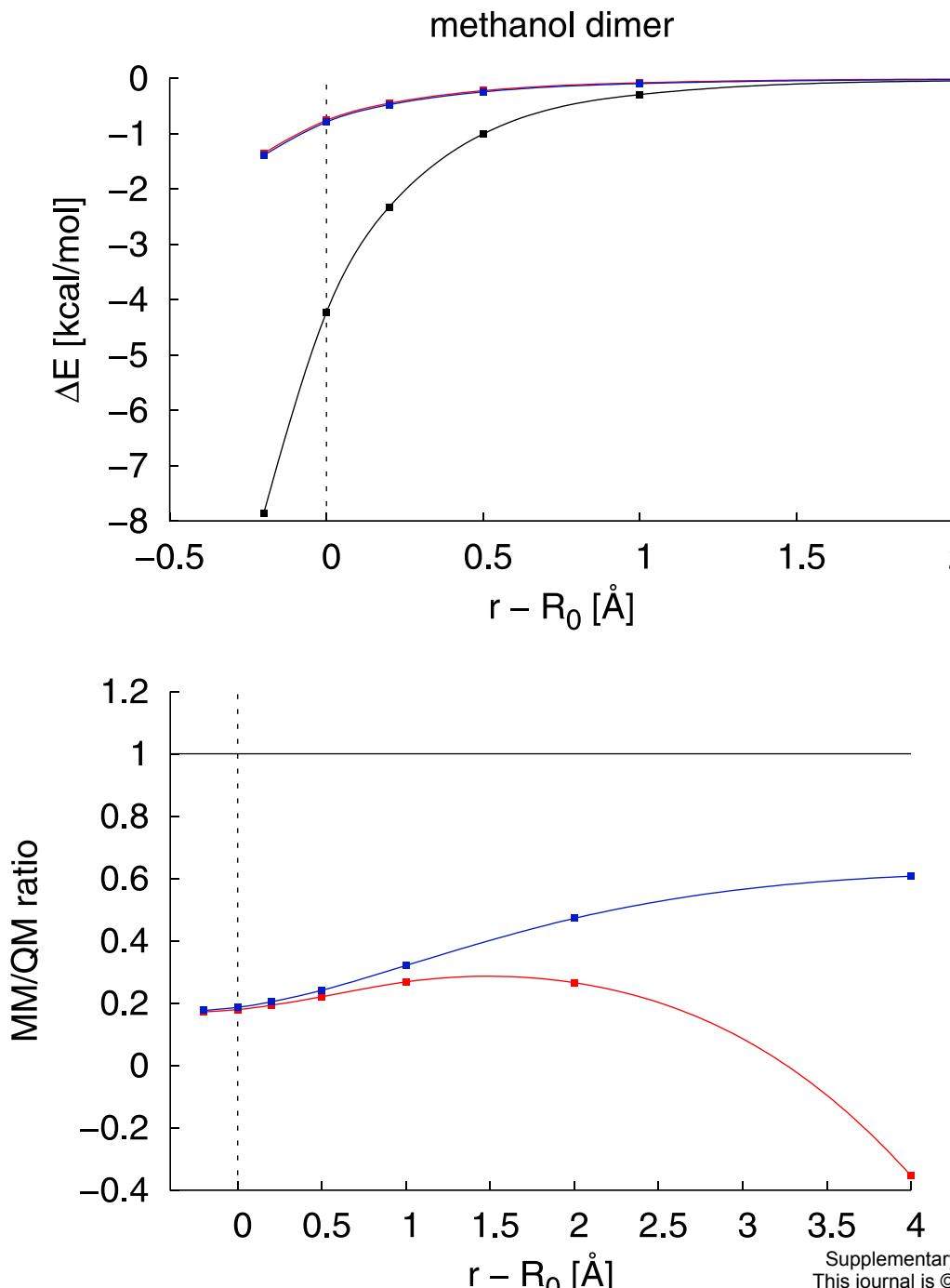
**Figure S4.** Polarization contributions to the interaction energies for the Cieplak *et al.* force field (MM, blue) and DFT-SAPT (QM, black) induction (top) and the MM/QM ratio (bottom). For comparison also the MM values and MM/QM ratios calculated with inclusion of the self-polarized dipole – self-polarized dipole electrostatic interaction are given (red). Zero on the *x* axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol.

The “EPOLAR” value in the sander output file includes also the direct electrostatic self-induced dipole – self-induced dipole interaction. The self-induced dipoles are dipoles induced within a molecule by its own charge distribution and they are a part of the permanent dipole moment. Therefore, strictly speaking, their mutual interaction should be considered a part of the electrostatic energy, not the polarization energy. Including them in the EPOLAR term makes this term often positive at larger intermolecular distances (red curves), although pure polarization energy should never be positive. Unfortunately, if we wanted to print out only that part of the polarization energy, which is due to the intermolecular polarization, source code modification would be required. However, this is not a problem when two atomic ions are interacting, because there is no self-polarization involved. Also in the case of very small molecules (with only 1-2 and 1-3 intra-molecular terms) the self-polarization is zero because the 1-2 and 1-3 interactions are excluded from calculation in sander. In yet larger molecules where also the 1-4 interactions contribute, like in methanol, methylamine, acetic acid and their ions, the 1-4 term already creates some self-polarization, although this is scaled down according to the value of the “SCEE” option in sander. In this particular case, “pure” polarization interaction can be estimated by setting SCEE very large, so that the intramolecular polarization is close to zero. This is how we estimated the intermolecular polarization in the following graphs (blue curves). If also the 1-5 interactions are present, as in the case of uracil, printing out the “pure” polarization values would be much more difficult and we did not attempt it.

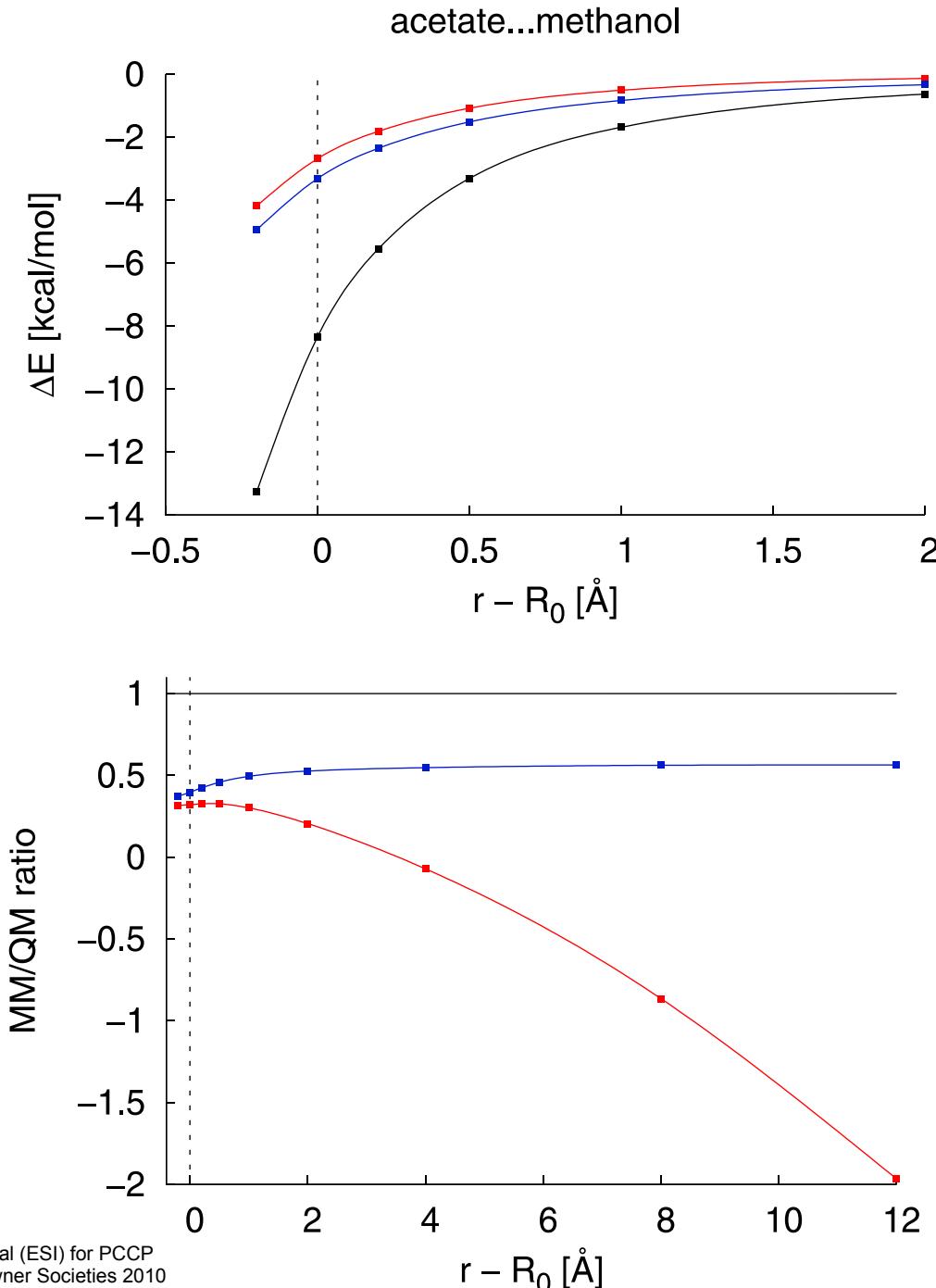
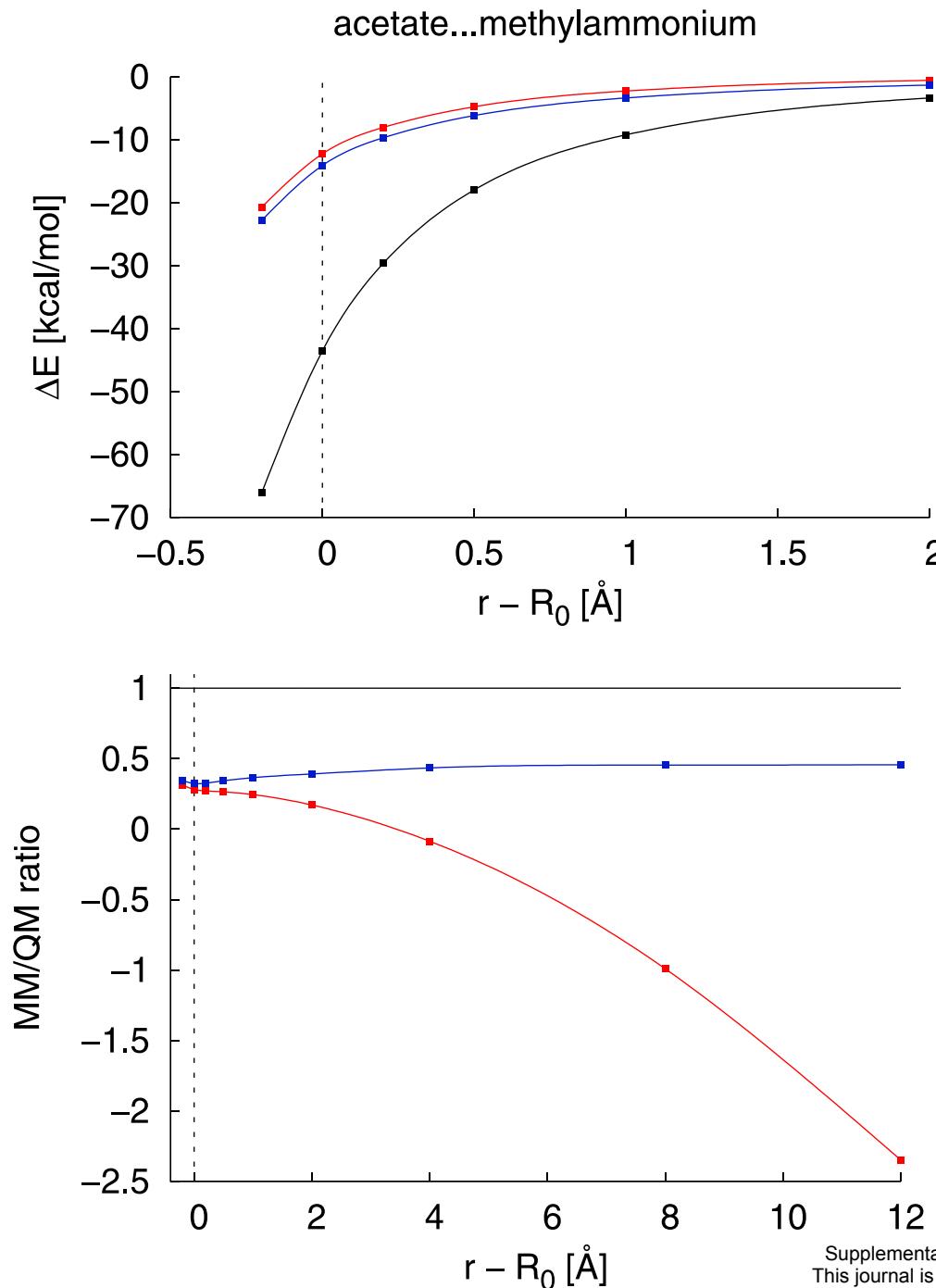
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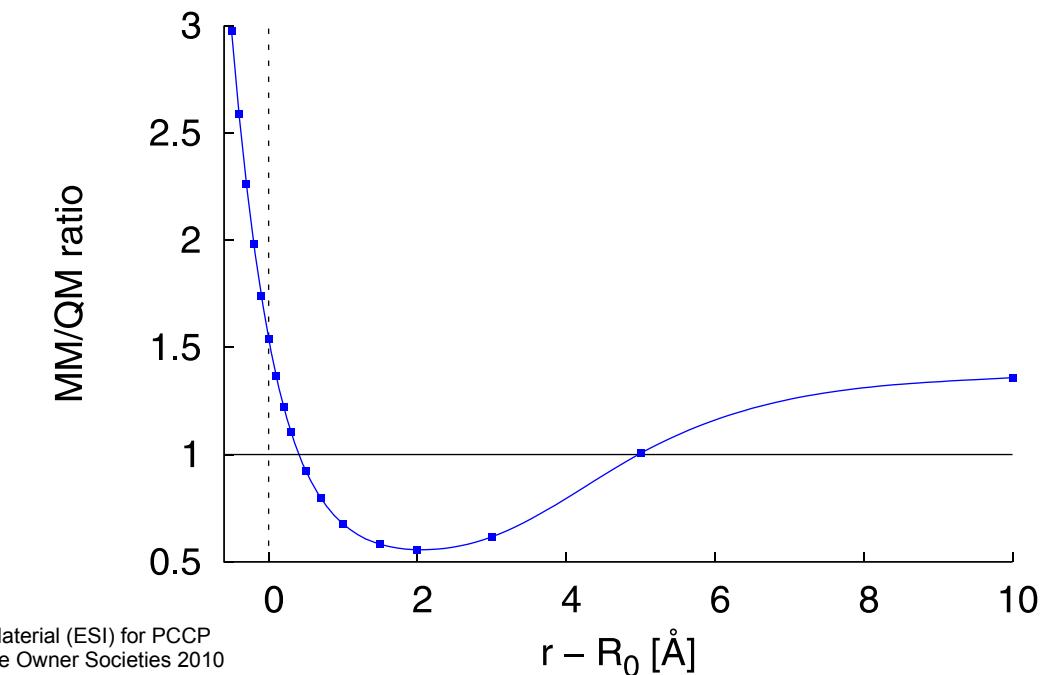
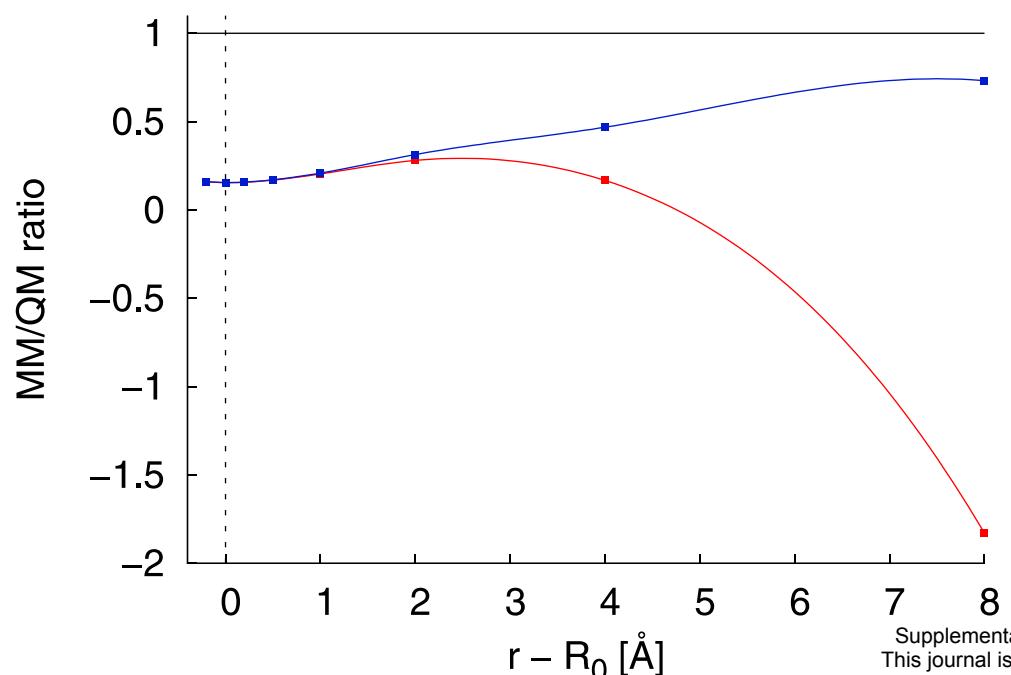
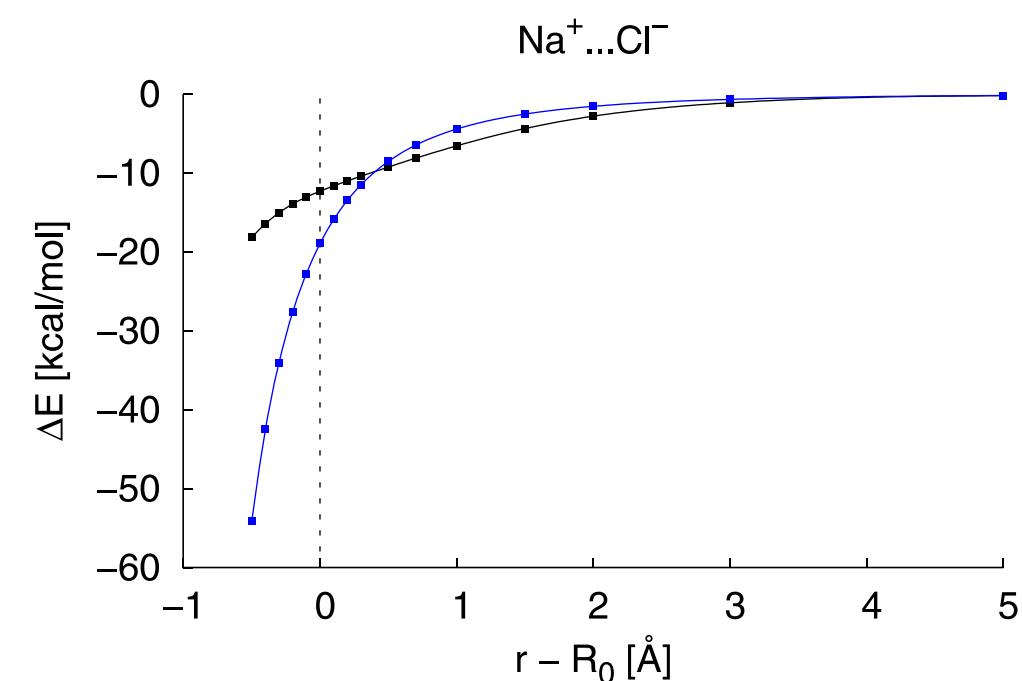
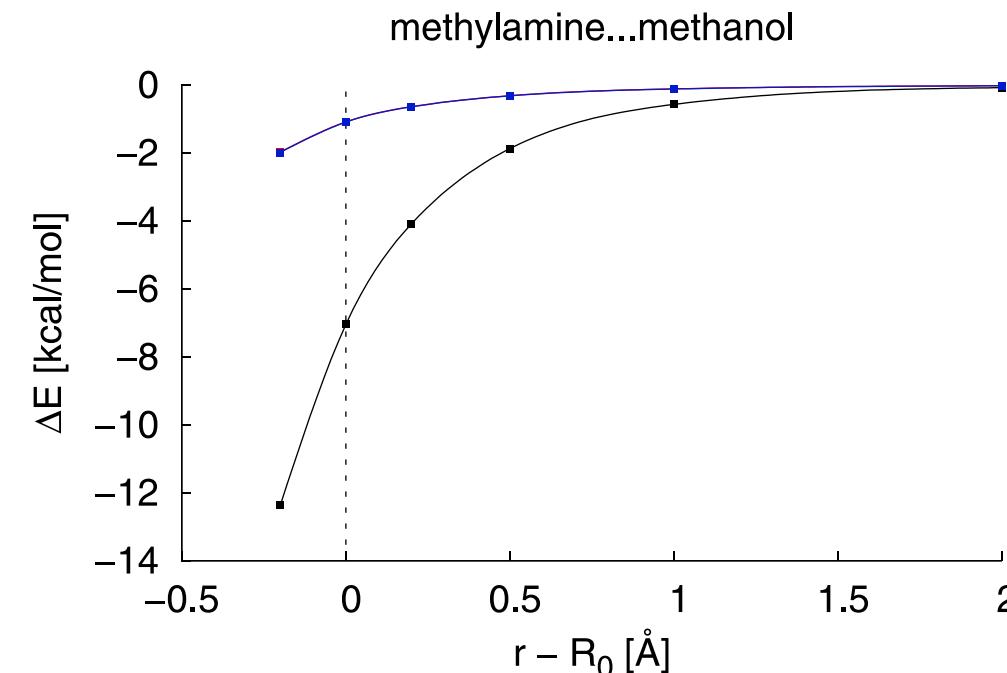
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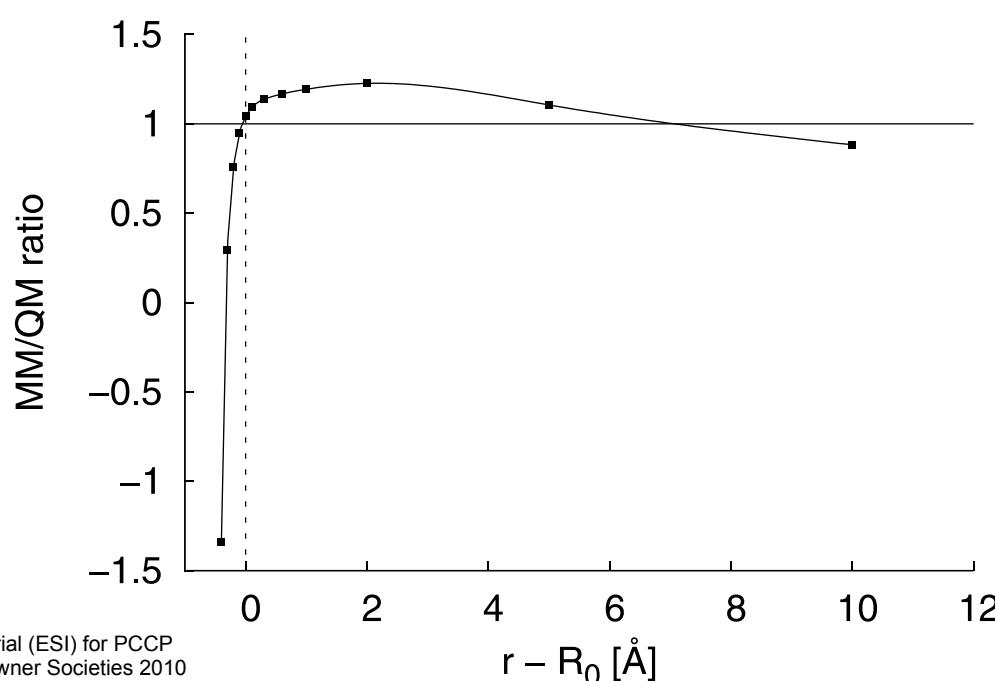
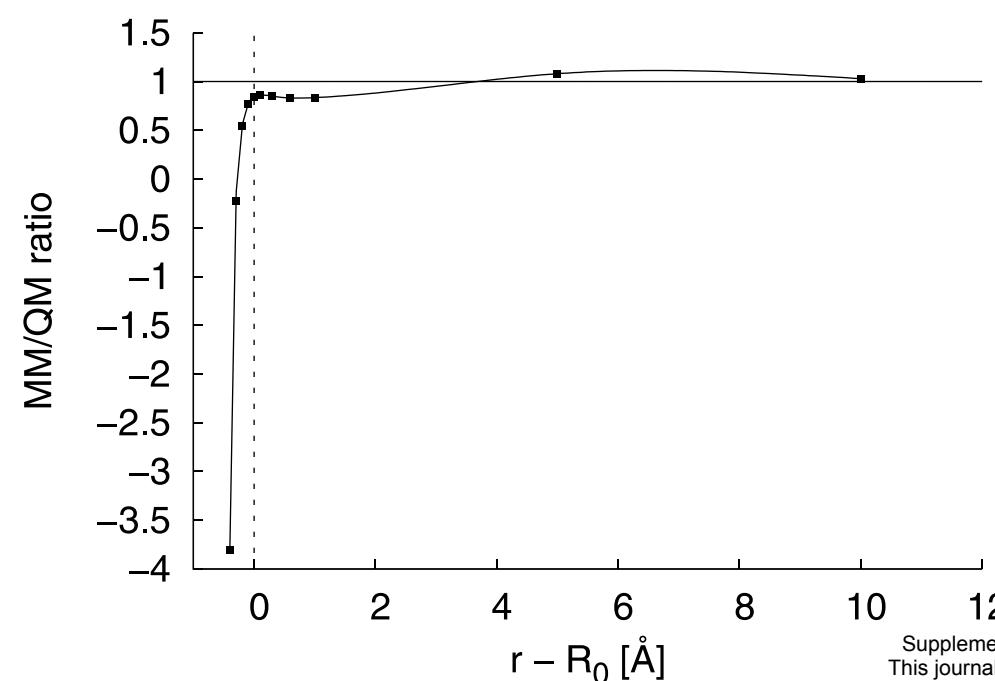
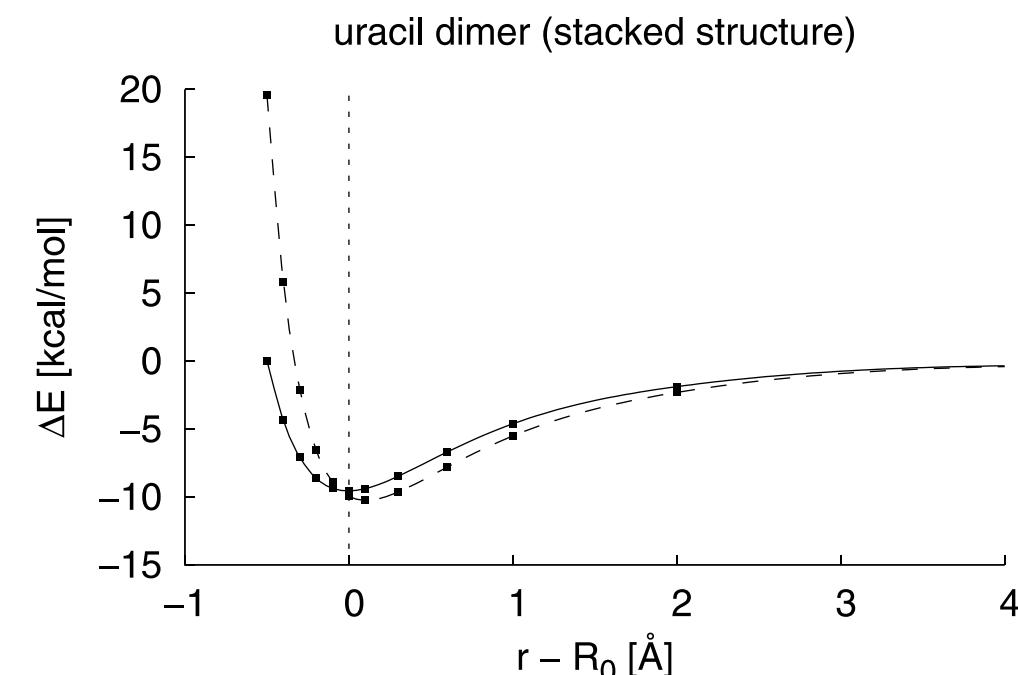
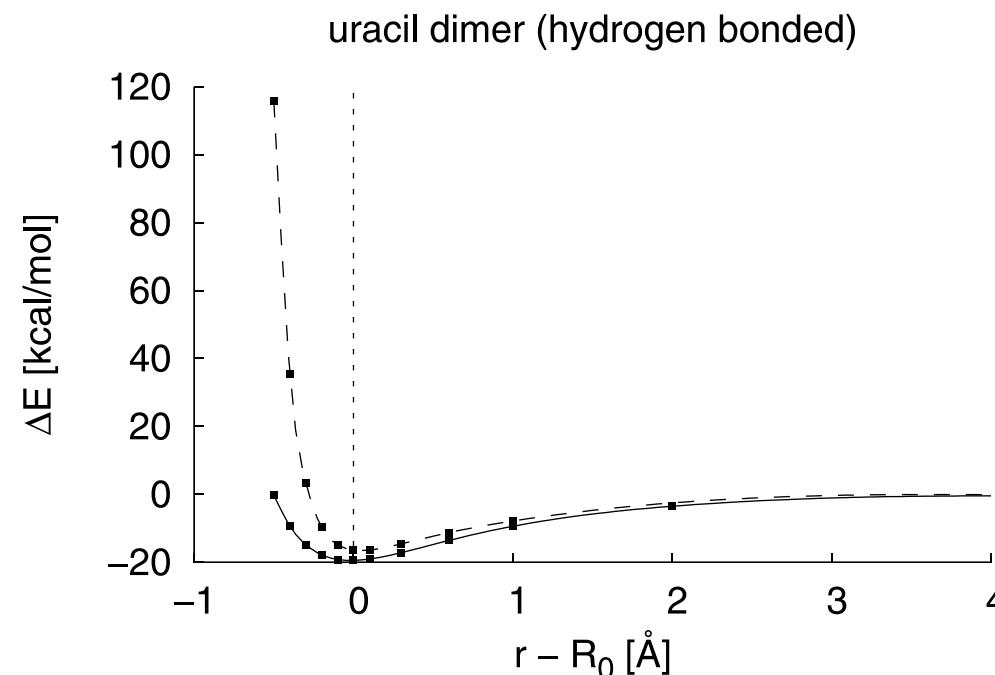
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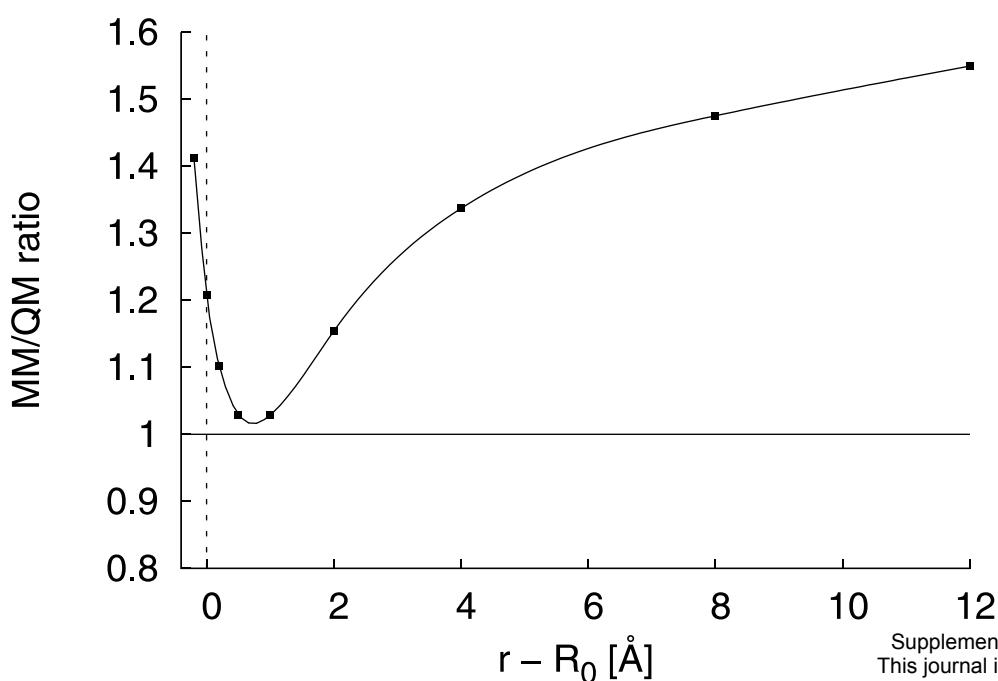
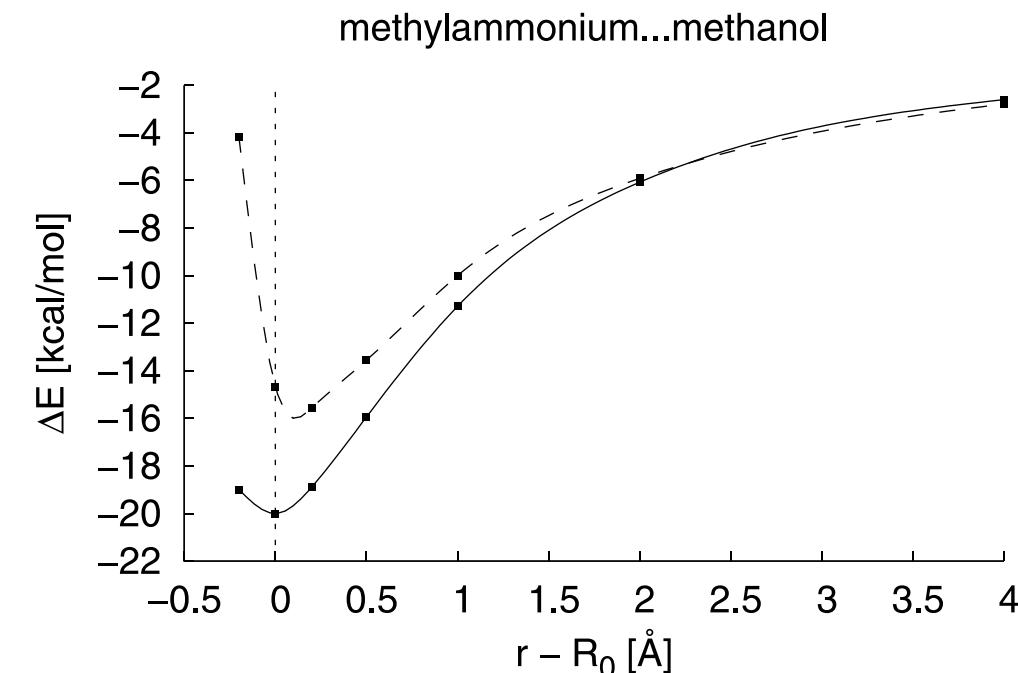
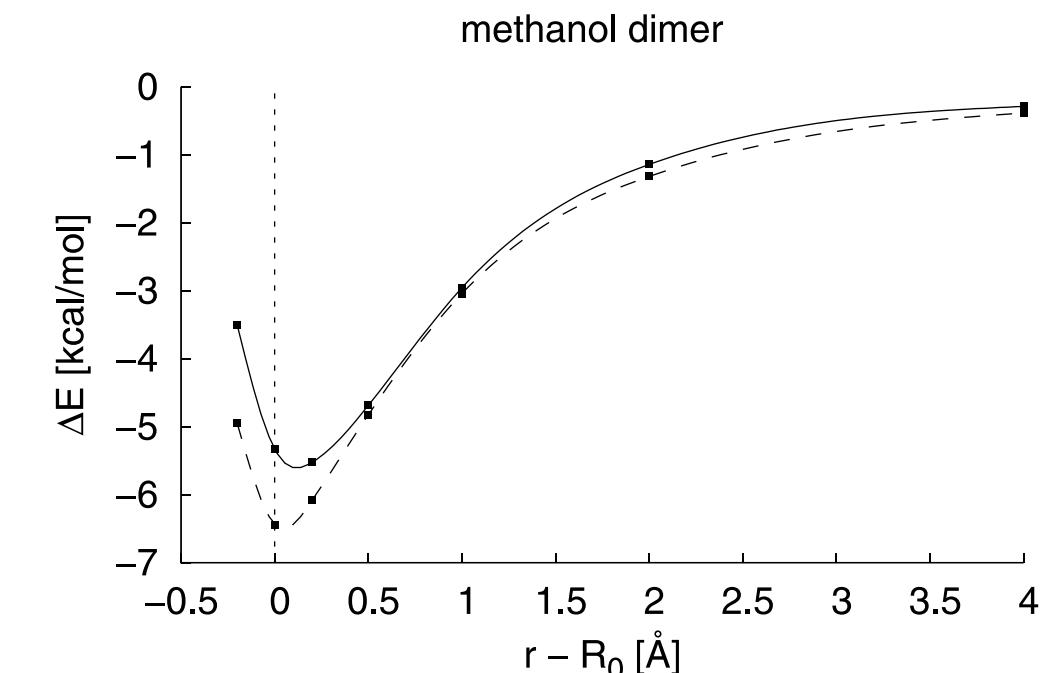
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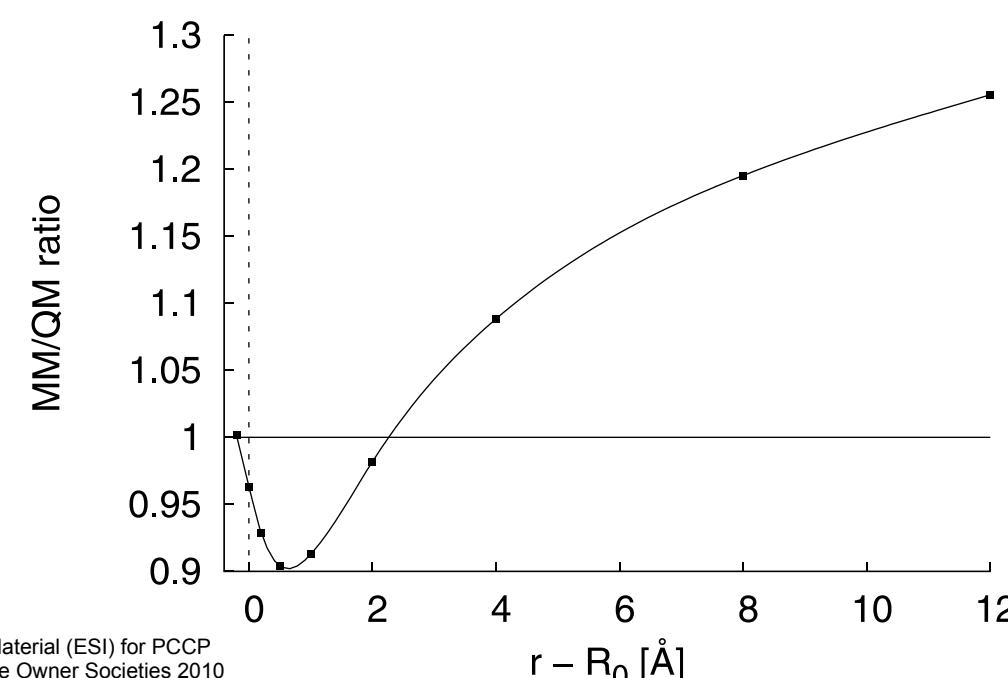
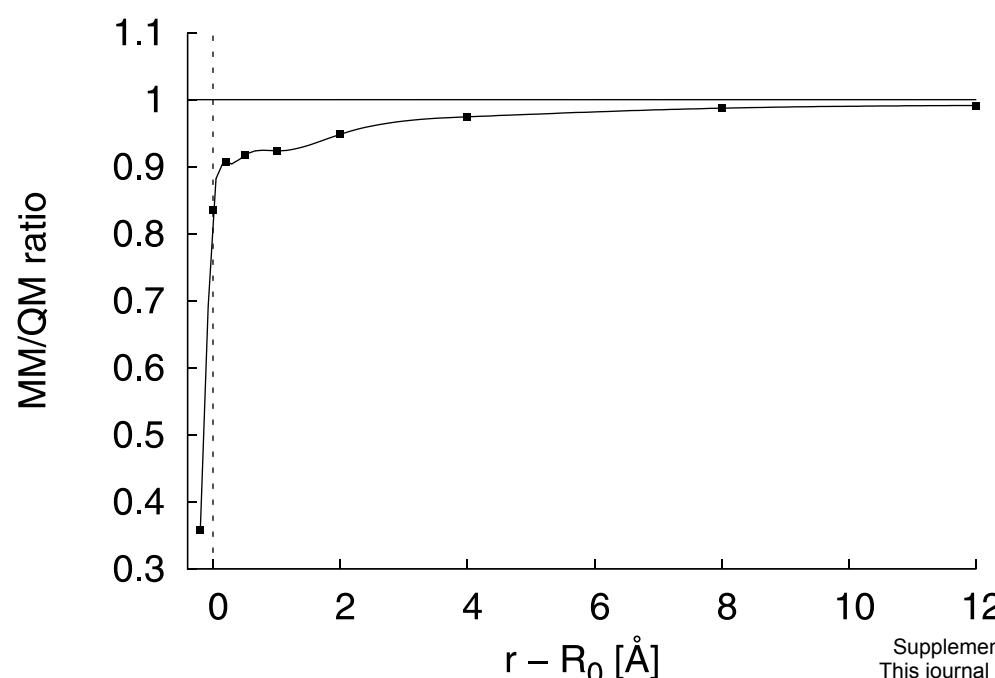
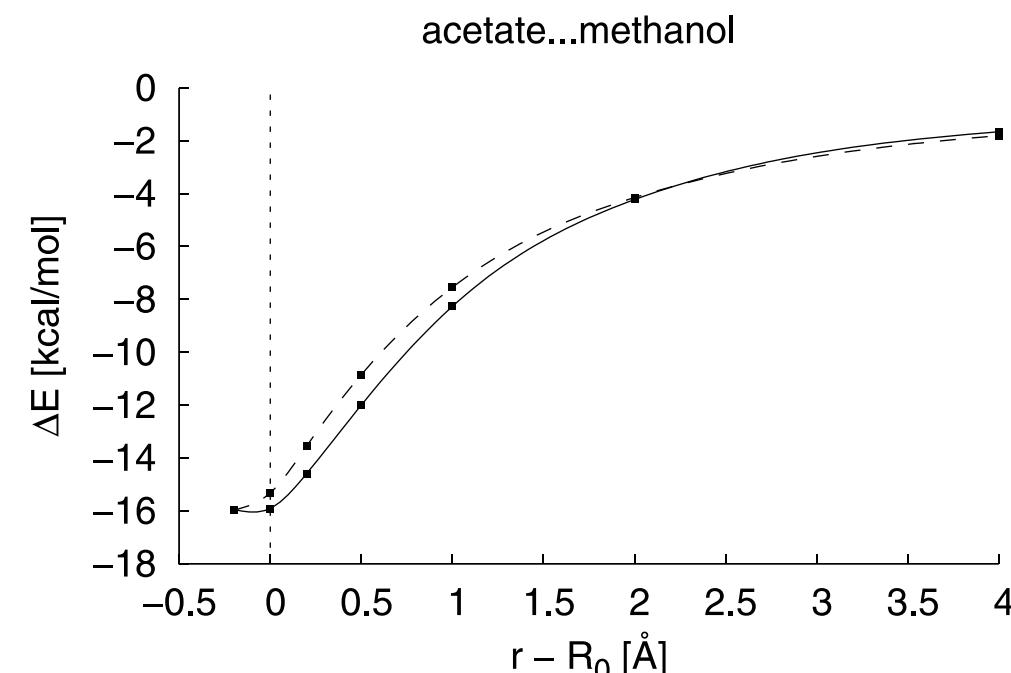
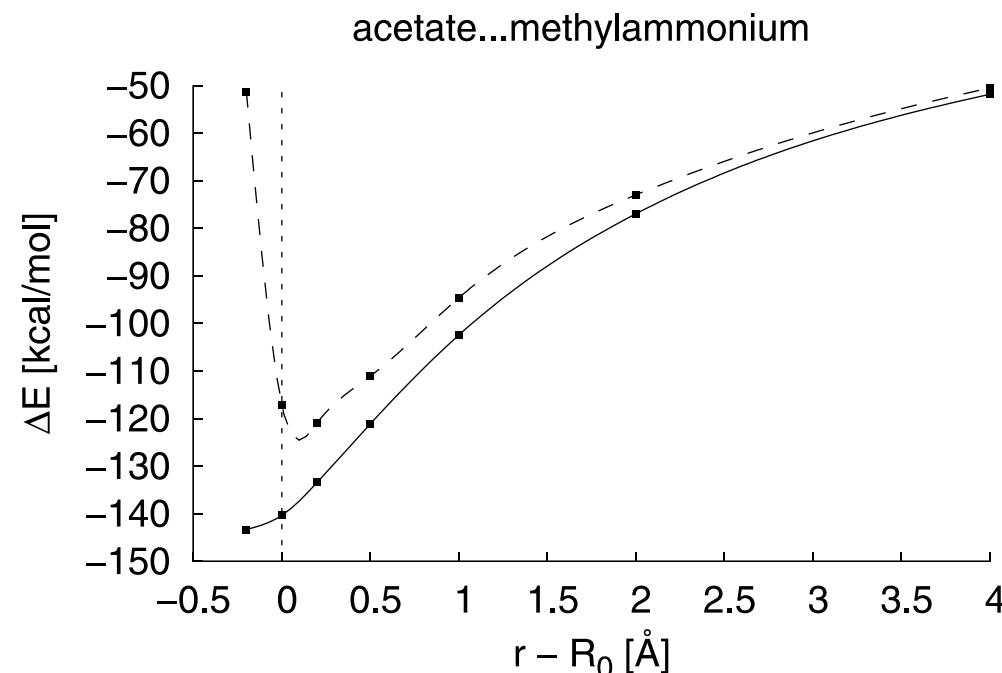
**Figure S5.** Total Cornell *et al.* force field (MM, dashed line) and DFT-SAPT (QM, full line) interaction energies (top) and MM/QM ratios (bottom). Zero on the *x* axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol.



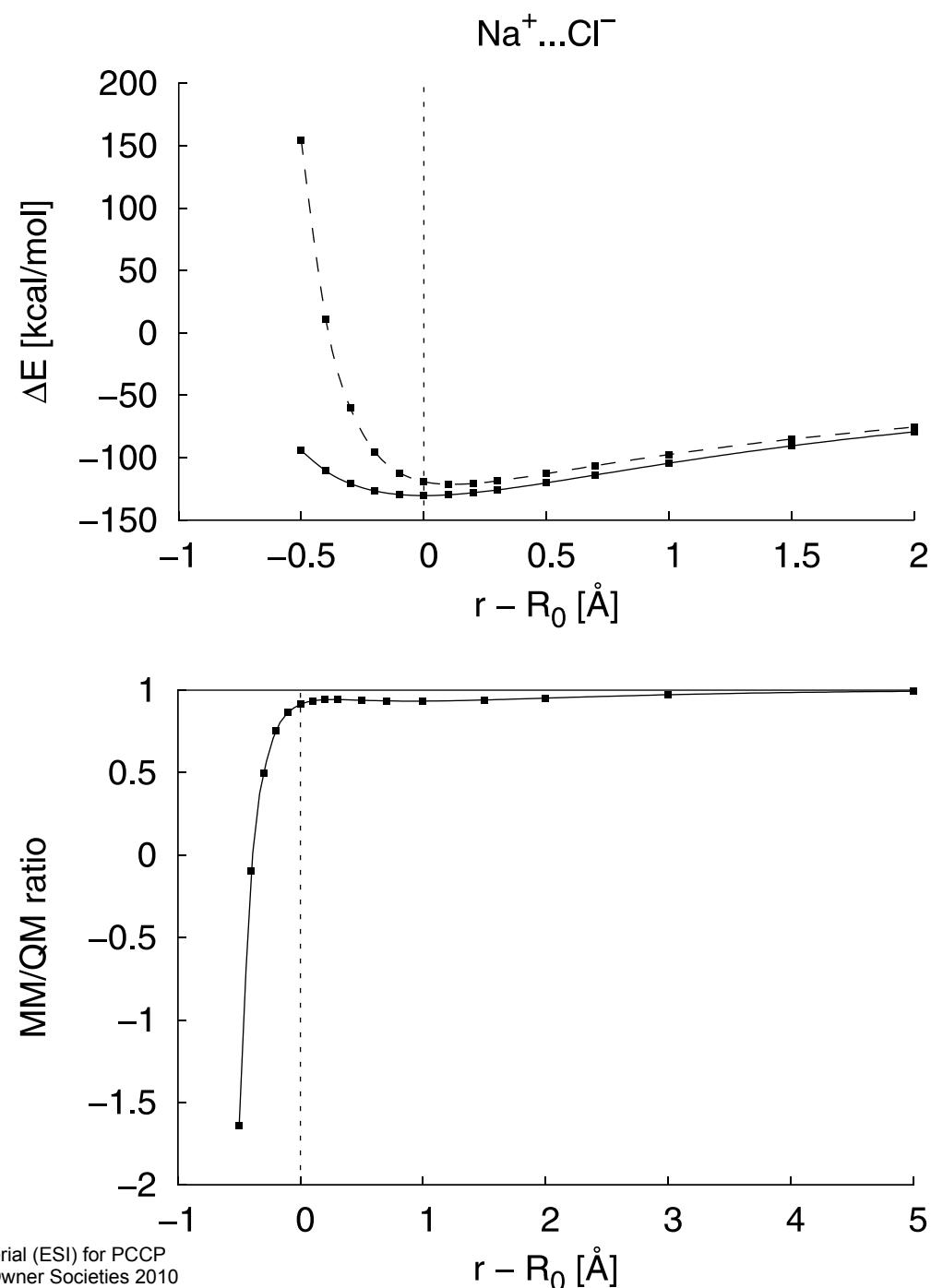
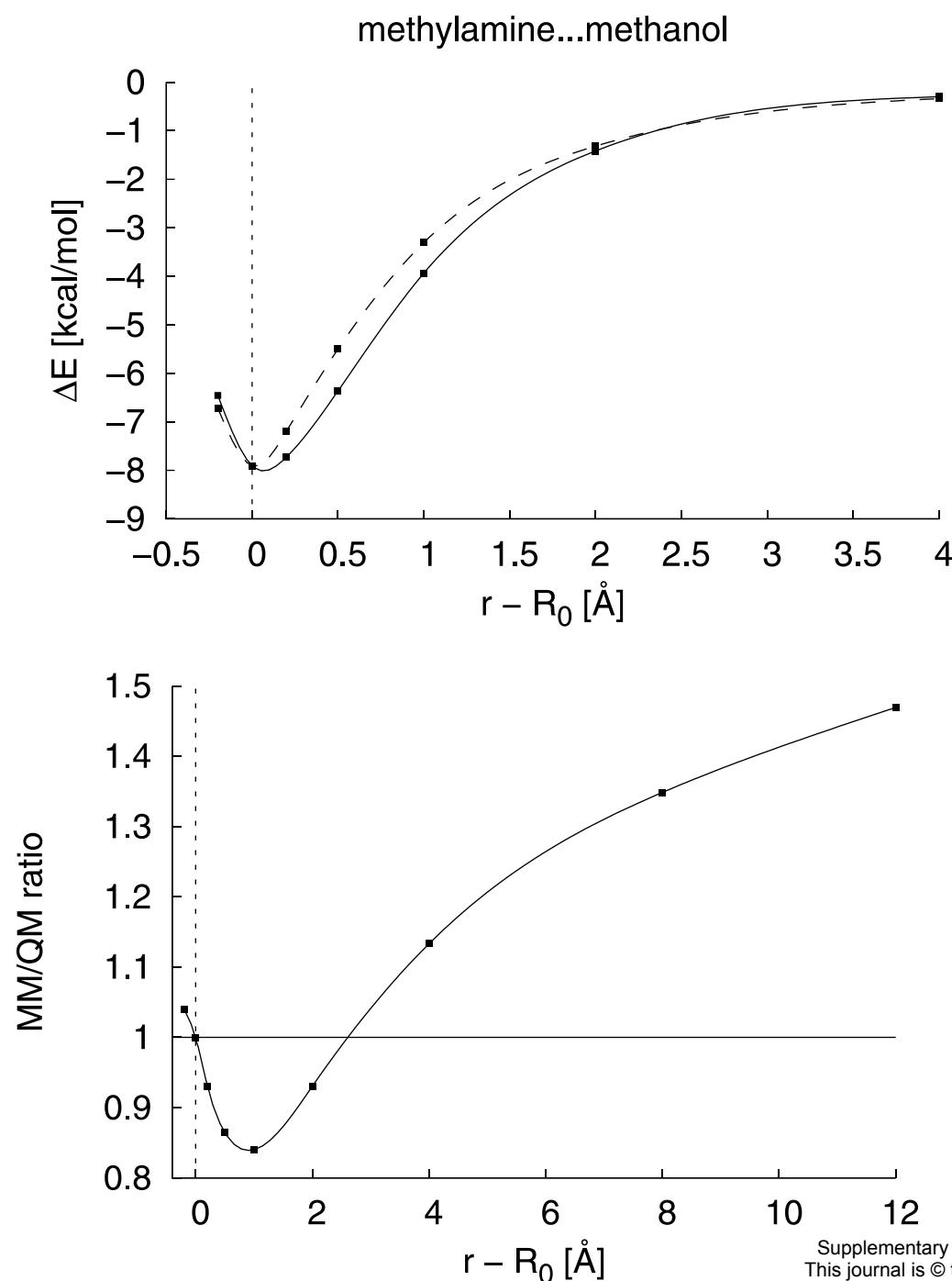
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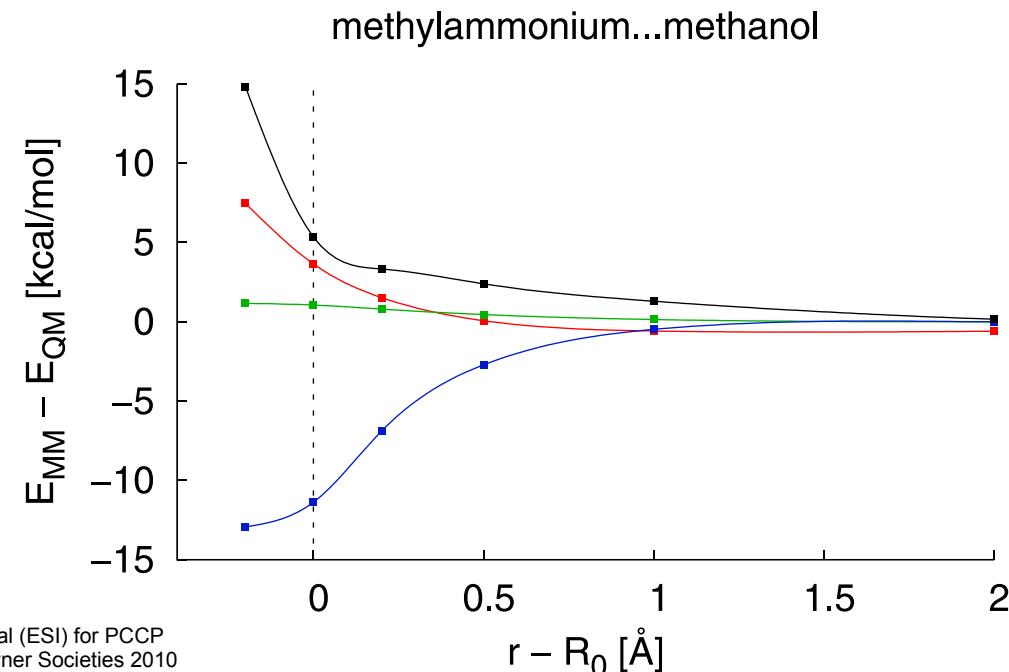
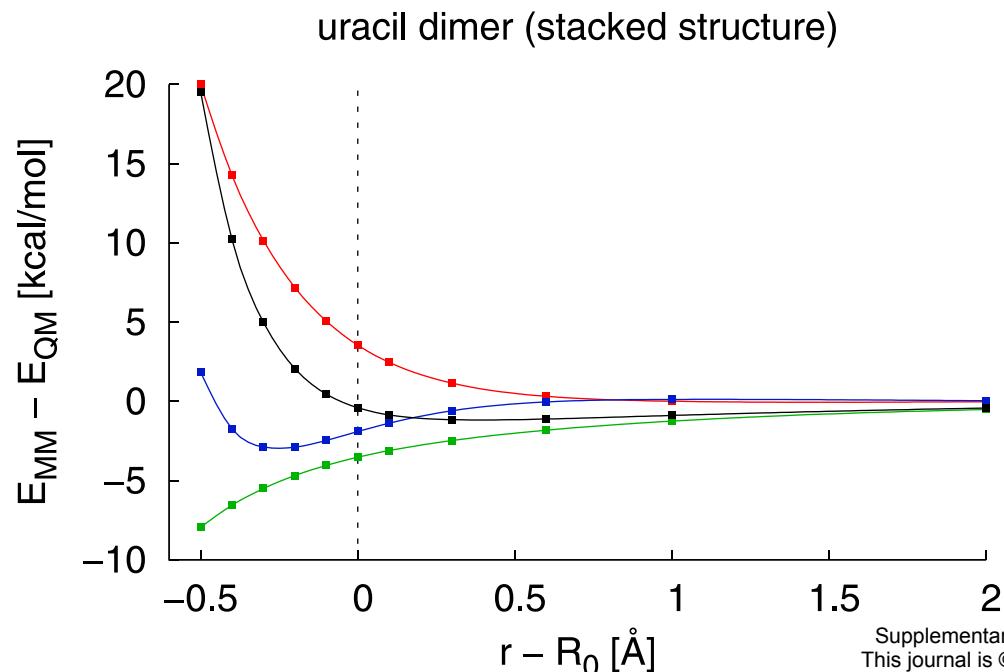
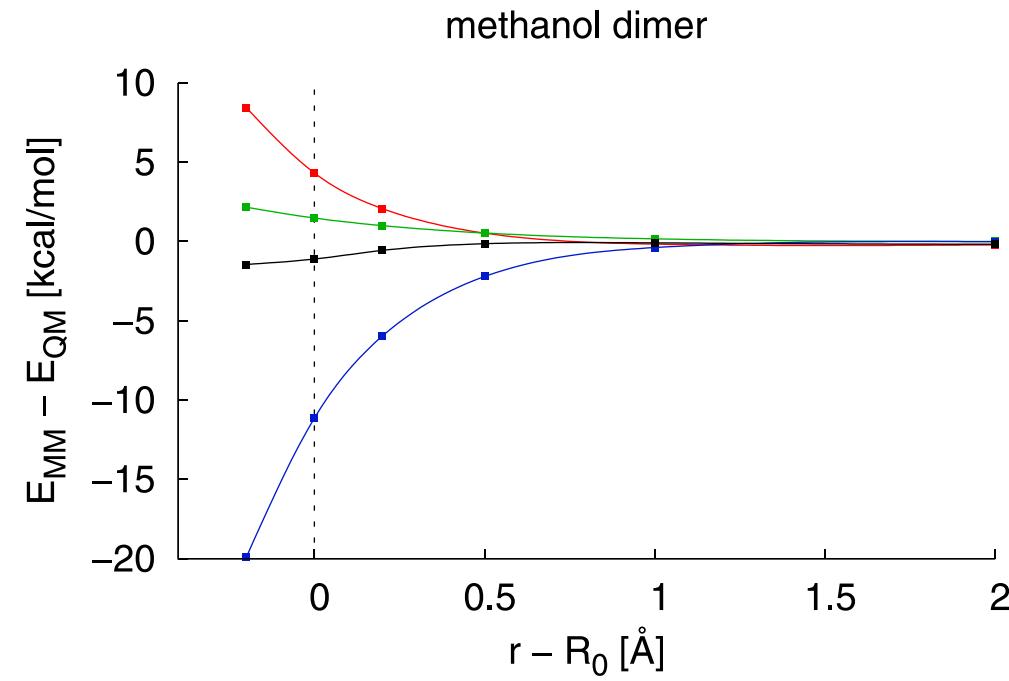
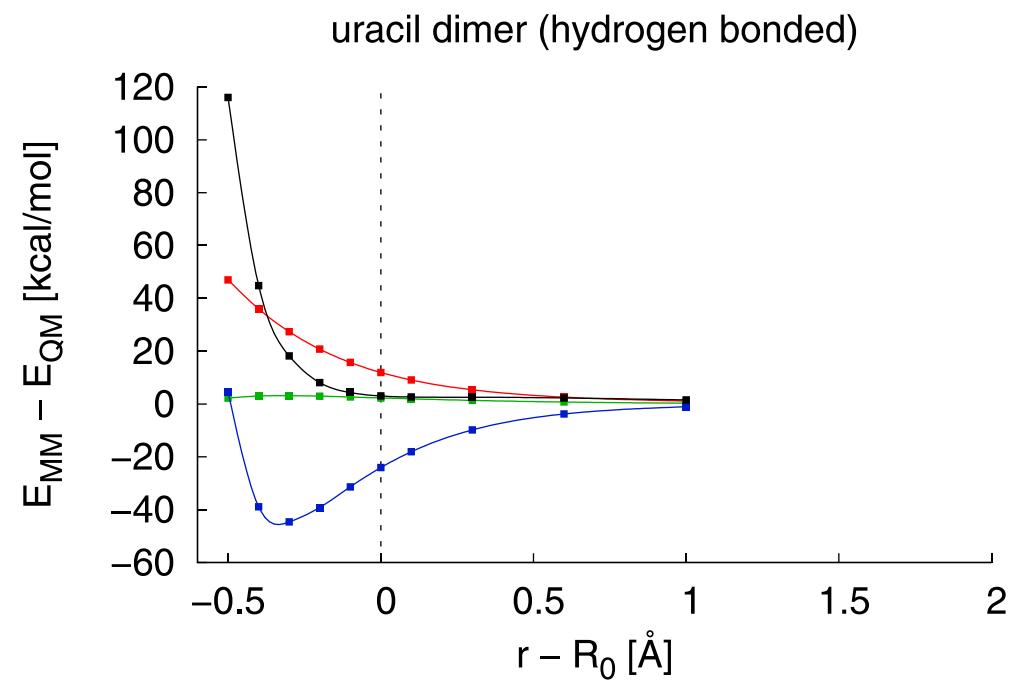
**Figure S5 (continuation).** Total Cornell *et al.* force field (MM, dashed line) and DFT-SAPT (QM, full line) interaction energies (top) and MM/QM ratios (bottom). Zero on the *x* axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol.



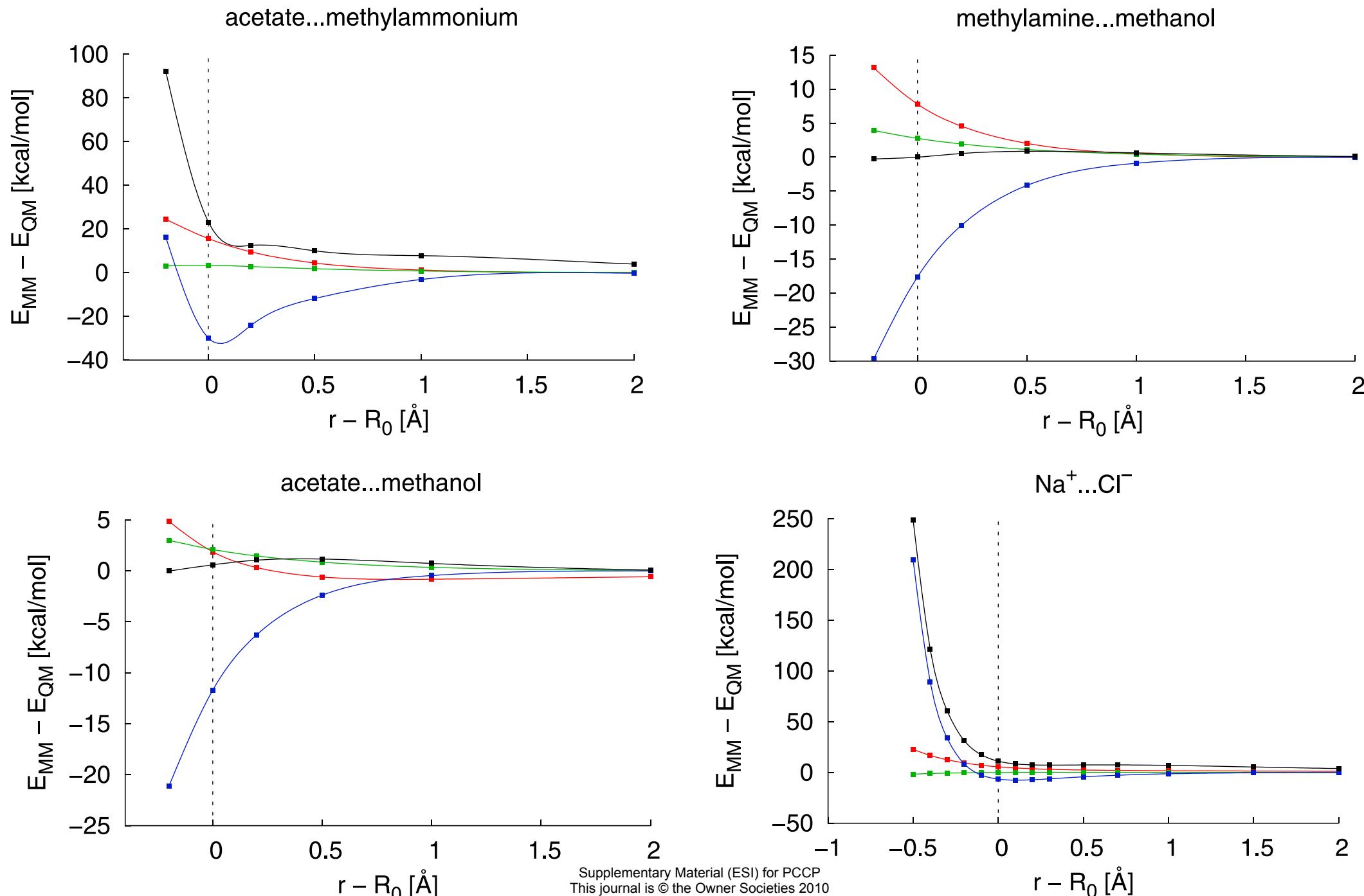
**Figure S5 (continuation).** Total Cornell *et al.* force field (MM, dashed line) and DFT-SAPT (QM, full line) interaction energies (top) and MM/QM ratios (bottom). Zero on the  $x$  axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol.



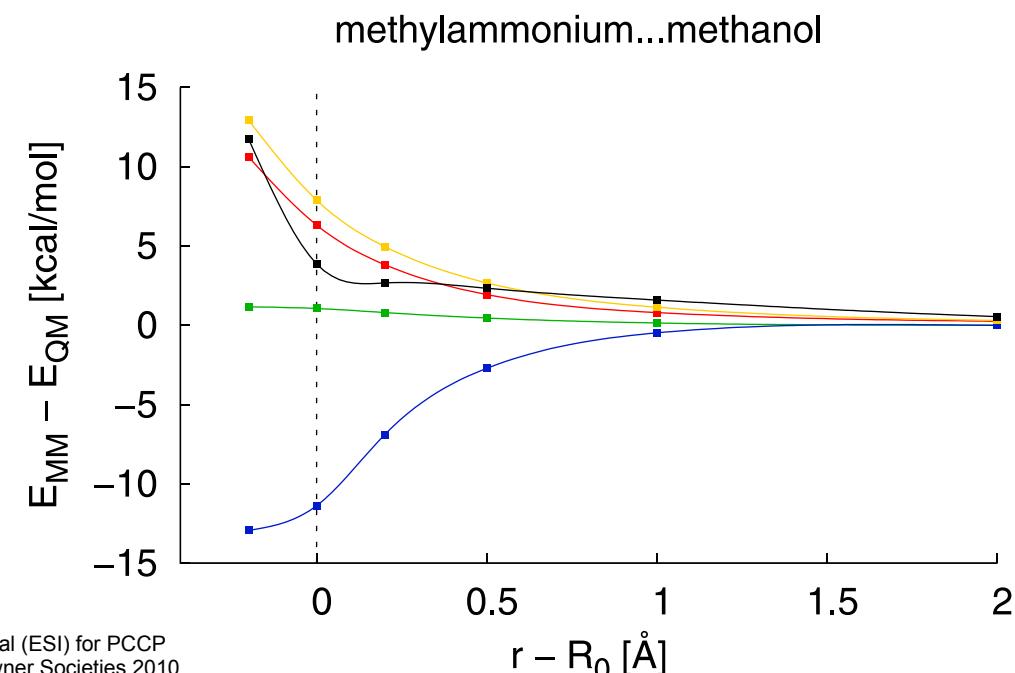
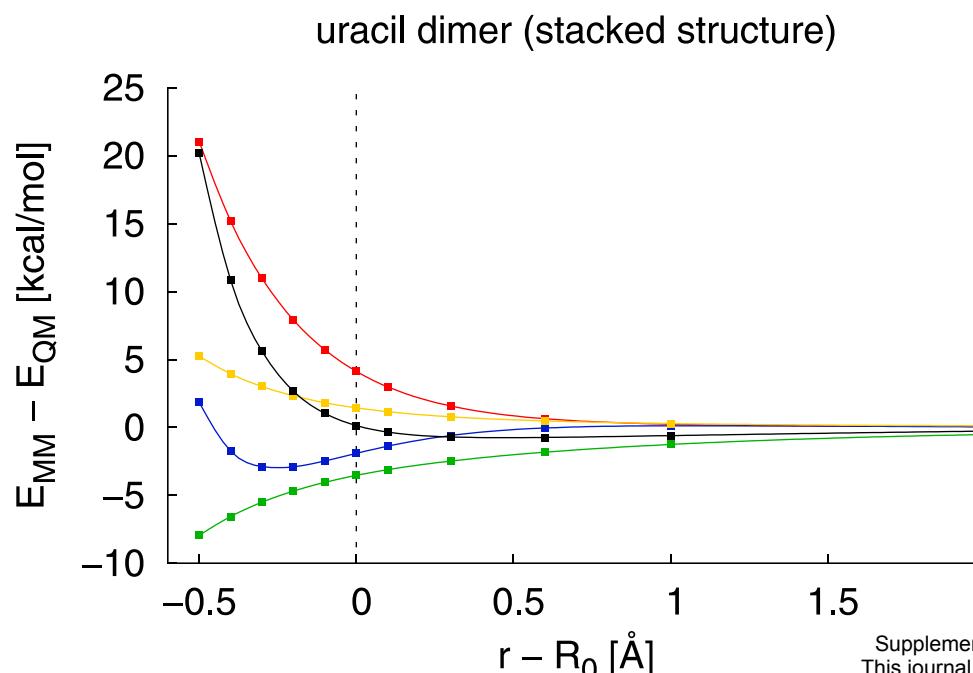
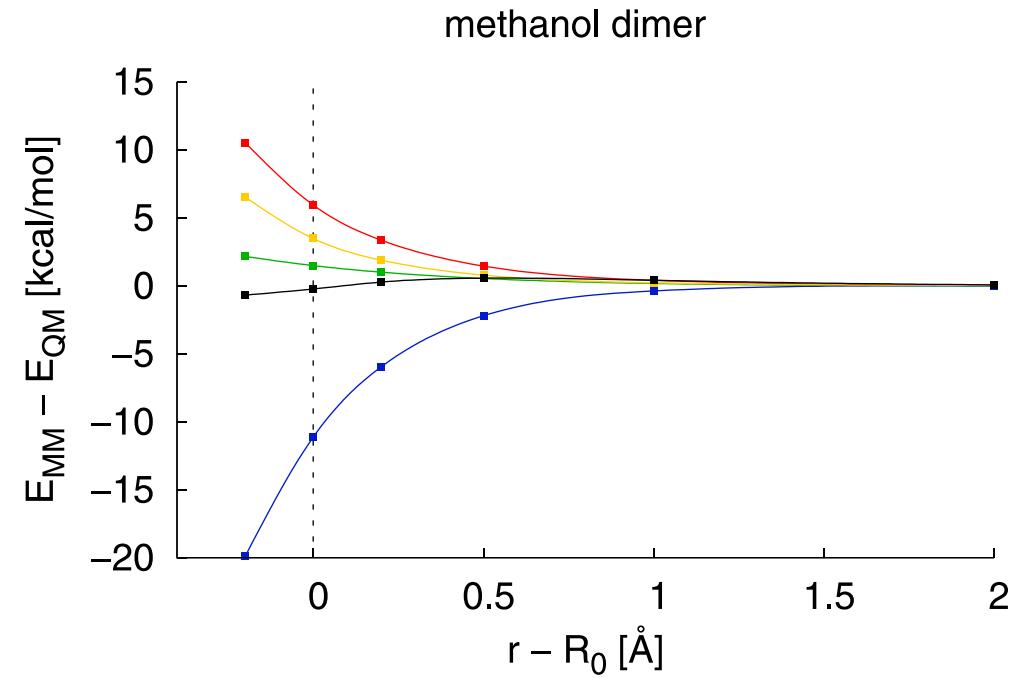
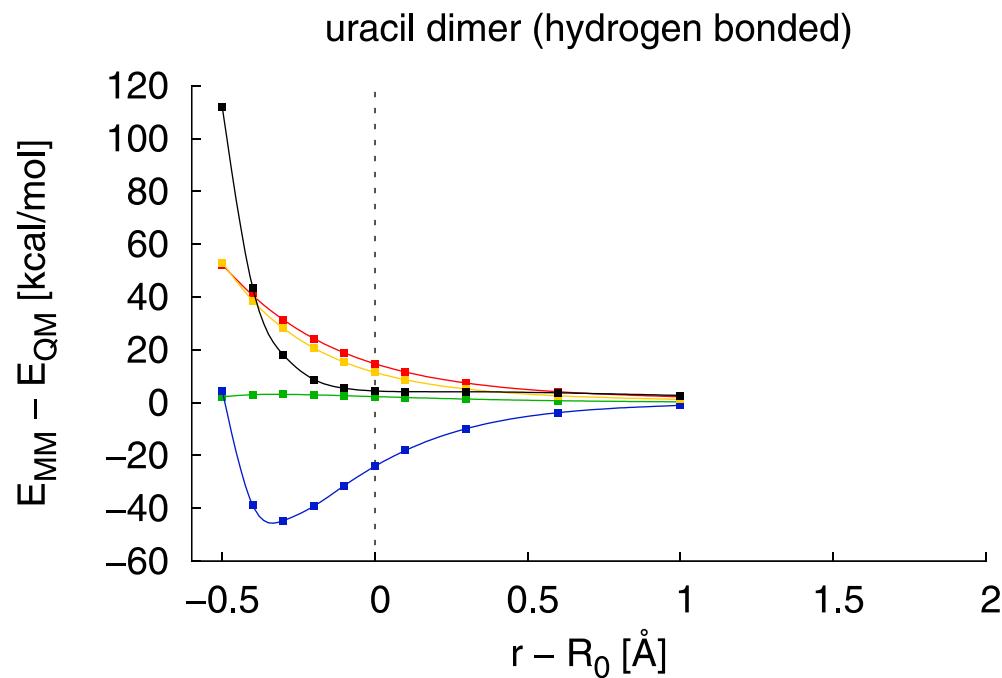
**Figure S6.** Absolute errors of the individual interaction energy components (kcal/mol) as a function of distance for Cornell *et al.* force field. Zero on the  $x$  axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol. Total error, black; electrostatic, red; repulsion, blue; dispersion, green. Note that for Cornell *et al.* force fields the total error (MM - QM) is not the sum of the component errors shown, because the induction component is not shown.



**Figure S6 (continuation).** Absolute errors of the individual interaction energy components (kcal/mol) as a function of distance for Cornell *et al.* force field. Zero on the  $x$  axis corresponds to the equilibrium distance  $R_0$ . Interaction energies in kcal/mol. Total error, black; electrostatic, red; repulsion, blue; dispersion, green. Note that for Cornell *et al.* force fields the total error (MM - QM) is not the sum of the component errors shown, because the induction component is not shown.



**Figure S7.** Absolute errors of the individual interaction energy components (kcal/mol) as a function of distance for polarizable Cieplak *et al.* force field (ff02). Zero on the  $x$  axis corresponds to the equilibrium distance. Interaction energies in kcal/mol. Total error, black; electrostatics, red; repulsion, blue; dispersion, green, induction, yellow.



**Figure S7 (continuation).** Absolute errors of the individual interaction energy components (kcal/mol) as a function of distance for polarizable Cieplak *et al.* force field (ff02). Zero on the  $x$  axis corresponds to the equilibrium distance. Interaction energies in kcal/mol. Total error, black; electrostatics, red; repulsion, blue; dispersion, green, induction,

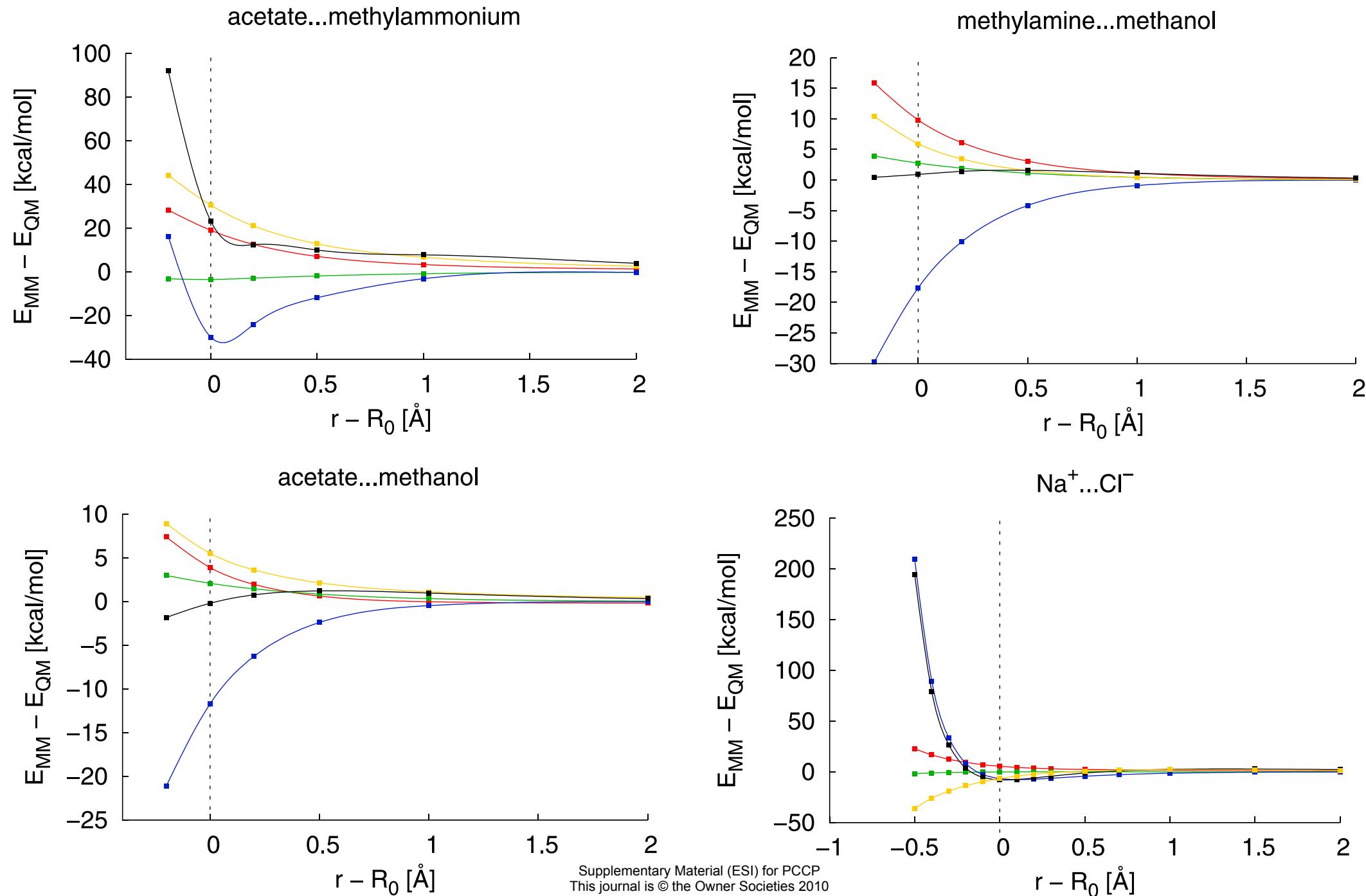


Table S1: DFT-SAPT and MM interaction energies for uracil dimer (hydrogen bonded structure). Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.5	-80.55	-62.22	-25.50	167.97	-0.29	-33.56	-28.28	-36.84	172.54	-23.26	115.72
-0.4	-65.23	-44.70	-20.62	121.22	-9.33	-29.22	-24.63	-32.13	82.30	-17.60	35.49
-0.3	-52.98	-32.31	-16.80	87.31	-14.79	-25.60	-21.58	-28.20	42.66	-13.66	3.41
-0.2	-43.31	-23.55	-13.79	62.84	-17.80	-22.56	-19.01	-24.87	23.66	-10.82	-9.71
-0.1	-35.69	-17.33	-11.37	45.23	-19.16	-19.97	-16.83	-22.04	13.86	-8.72	-14.83
0.0	-29.70	-12.88	-9.42	32.57	-19.44	-17.76	-14.96	-19.62	8.48	-7.13	-16.40
0.1	-24.96	-9.67	-7.85	23.45	-19.03	-15.86	-13.35	-17.52	5.38	-5.89	-16.37
0.3	-18.16	-5.64	-5.51	12.16	-17.14	-12.78	-10.73	-14.13	2.35	-4.14	-14.57
0.6	-12.07	-2.71	-3.33	4.56	-13.54	-9.47	-7.92	-10.46	0.79	-2.58	-11.25
1.0	-7.69	-1.16	-1.78	1.25	-9.38	-6.58	-5.47	-7.25	0.22	-1.48	-7.83
2.0	-3.23	-0.22	----	0.05	----	-3.04	-2.49	-3.32	0.02	-0.47	-3.49
5.0	-0.58	-0.01	----	0.00	----	-0.60	-0.47	-0.62	0.00	-0.04	-0.64
10.0	-0.10	0.00	0.00	0.00	-0.10	-0.10	-0.08	-0.10	0.00	0.00	-0.10

- a) Cornell *et al* force field, RESP HF/6-31G\* charges are used.
- b) Cieplak *et al* force field, RESP B3LYP/cc-pVTZ charges are used.
- c) Duan *et al* force field, RESP B3LYP/cc-pVTZ/ $\varepsilon = 4.0$  charges are used

\* DFT-SAPT calculation of dispersion failed

Table S2: DFT-SAPT and MM interaction energies for uracil dimer (stacked structure). Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.5	-28.63	-5.65	-24.96	59.26	3.54	-8.64	-7.58	-10.38	61.11	-32.91	19.56
-0.4	-22.03	-4.25	-21.17	43.09	-1.65	-7.76	-6.83	-9.38	41.35	-27.73	5.86
-0.3	-17.13	-3.22	-18.00	31.27	-5.03	-6.98	-6.16	-8.50	28.39	-23.50	-2.10
-0.2	-13.49	-2.46	-15.32	22.65	-7.09	-6.31	-5.57	-7.72	19.76	-20.01	-6.56
-0.1	-10.77	-1.90	-13.07	16.38	-8.21	-5.71	-5.05	-7.03	13.92	-17.11	-8.91
0.0	-8.72	-1.49	-11.17	11.83	-8.69	-5.18	-4.59	-6.41	9.92	-14.70	-9.96
0.1	-7.17	-1.18	-9.57	8.52	-8.74	-4.71	-4.18	-5.86	7.14	-12.67	-10.25
0.3	-5.07	-0.76	-7.06	4.41	-8.11	-3.92	-3.49	-4.92	3.81	-9.53	-9.64
0.6	-3.34	-0.43	-4.55	1.62	-6.51	-3.02	-2.69	-3.84	1.59	-6.37	-7.81
1.0	-2.19	-0.23	-2.62	0.42	-4.54	-2.18	-1.95	-2.82	0.54	-3.87	-5.51
2.0	-1.04	-0.07	-0.78	0.01	-1.86	-1.07	-0.96	-1.43	0.05	-1.29	-2.31
5.0	-0.23	-0.01	-0.06	0.00	-0.29	-0.22	-0.20	-0.32	0.00	-0.11	-0.33
10.0	-0.05	0.00	0.00	0.00	-0.05	-0.04	-0.04	-0.07	0.00	-0.01	-0.05

- a) Cornell *et al* force field, RESP HF/6-31G\* charges are used.
- b) Cieplak *et al* force field, RESP B3LYP/cc-pVTZ charges are used.
- c) Duan *et al* force field, RESP B3LYP/cc-pVTZ/ $\epsilon = 4.0$  charges are used

Table S3: DFT-SAPT and MM interaction energies for methanol dimer. Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{ind}}^{\text{MMd)}$	$E_{\text{ind}}^{\text{MMe)}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.2	-17.84	-7.86	-6.66	28.86	-3.51	-9.41	-7.31	-8.97	8.96	-4.51	-1.35	-1.39	-4.95
0	-11.62	-4.23	-4.56	15.07	-5.33	-7.30	-5.68	-6.97	3.94	-3.07	-0.76	-0.79	-6.44
0.2	-7.83	-2.33	-3.14	7.78	-5.53	-5.76	-4.49	-5.50	1.82	-2.14	-0.45	-0.48	-6.09
0.5	-4.68	-1.00	-1.83	2.83	-4.69	-4.15	-3.23	-3.97	0.63	-1.30	-0.22	-0.24	-4.83
1	-2.39	-0.29	-0.78	0.51	-2.96	-2.56	-1.99	-2.45	0.13	-0.61	-0.08	-0.09	-3.04
2	-0.94	-0.04	-0.18	0.02	-1.14	-1.16	-0.90	-1.11	0.01	-0.17	-0.01	-0.02	-1.32
4	-0.27	0.00	-0.02	0.00	-0.29	-0.36	-0.28	-0.35	0.00	-0.03	0.00	0.00	-0.39
8	-0.05	0.00	0.00	0.00	-0.06	-0.08	-0.06	-0.08	0.00	0.00	0.00	0.00	-0.08
12	-0.02	0.00	0.00	0.00	-0.02	-0.03	-0.02	-0.03	0.00	0.00	0.00	0.00	-0.03

Table S4: DFT-SAPT and MM interaction energies for methylammonium...methanol. Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{ind}}^{\text{MMd)}$	$E_{\text{ind}}^{\text{MMe)}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.2	-30.12	-19.15	-7.30	37.58	-18.99	-22.66	-19.52	-21.92	24.64	-6.15	-6.10	-5.86	-4.17
0	-22.69	-12.03	-4.87	19.58	-20.00	-19.05	-16.38	-18.39	8.20	-3.82	-4.08	-3.88	-14.66
0.2	-17.75	-7.91	-3.29	10.06	-18.89	-16.23	-13.94	-15.64	3.16	-2.49	-2.92	-2.74	-15.56
0.5	-13.13	-4.59	-1.86	3.63	-15.95	-13.07	-11.20	-12.55	0.92	-1.41	-1.91	-1.76	-13.56
1	-8.96	-2.22	-0.76	0.64	-11.30	-9.54	-8.16	-9.13	0.16	-0.62	-1.09	-0.97	-10.00
2	-5.16	-0.77	-0.16	0.02	-6.08	-5.76	-4.91	-5.47	0.01	-0.17	-0.47	-0.39	-5.92
4	-2.40	-0.19	-0.02	0.00	-2.61	-2.77	-2.36	-2.61	0.00	-0.02	-0.15	-0.10	-2.80
8	-0.90	-0.03	0.00	0.00	-0.94	-1.07	-0.91	-0.99	0.00	0.00	-0.04	-0.02	-1.07
12	-0.47	-0.01	0.00	0.00	-0.48	-0.56	-0.48	-0.52	0.00	0.00	-0.02	-0.01	-0.56

- a) Cornell *et al* force field, RESP HF/6-31G\* charges are used.
- b) Cieplak *et al* force field, RESP B3LYP/cc-pVTZ charges are used.
- c) Duan *et al* force field, RESP B3LYP/cc-pVTZ/ $\varepsilon = 4.0$  charges are used
- d) polarization contribution including self-polarized dipoles
- e) polarization contribution without self-polarized dipoles

Table S5: DFT-SAPT and MM interaction energies for acetate...methylammonium. Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{ind}}^{\text{MMd)}$	$E_{\text{ind}}^{\text{MMe)}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.2	-163.86	-66.12	-17.29	103.97	-143.31	-139.40	-135.54	-142.29	120.23	-14.15	-20.73	-22.82	-33.31
0	-144.14	-43.54	-11.82	59.15	-140.35	-128.51	-125.07	-131.07	29.24	-8.40	-12.25	-14.09	-107.67
0.2	-128.94	-29.66	-8.18	33.38	-133.40	-119.36	-116.28	-121.65	9.28	-5.36	-8.05	-9.69	-115.43
0.5	-112.48	-17.96	-4.82	14.14	-121.12	-108.00	-105.35	-109.94	2.34	-2.97	-4.76	-6.16	-108.64
1	-94.59	-9.21	-2.10	3.46	-102.44	-93.34	-91.22	-94.85	0.38	-1.29	-2.26	-3.37	-94.25
2	-73.37	-3.36	-0.47	0.24	-76.96	-73.41	-71.96	-74.40	0.02	-0.34	-0.58	-1.32	-73.72
4	-51.03	-0.77	-0.05	0.00	-51.85	-51.27	-50.48	-51.79	0.00	-0.05	0.07	-0.34	-51.32
8	-31.68	-0.12	0.00	0.00	-31.80	-31.83	-31.49	-32.05	0.00	0.00	0.12	-0.05	-31.84
12	-22.95	-0.03	0.00	0.00	-22.98	-23.04	-22.85	-23.16	0.00	0.00	0.08	-0.02	-23.04

Table S6: DFT-SAPT and MM interaction energies for acetate...methanol. Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{ind}}^{\text{MMd)}$	$E_{\text{ind}}^{\text{MMe)}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.2	-24.28	-13.26	-6.67	28.26	-15.95	-19.45	-16.89	-19.94	7.16	-3.68	-4.18	-4.94	-15.97
0	-17.74	-8.34	-4.58	14.76	-15.91	-15.88	-13.85	-16.34	3.06	-2.50	-2.68	-3.31	-15.32
0.2	-13.51	-5.55	-3.20	7.67	-14.59	-13.19	-11.54	-13.62	1.38	-1.74	-1.81	-2.35	-13.55
0.5	-9.64	-3.31	-1.90	2.85	-11.99	-10.25	-9.01	-10.63	0.46	-1.06	-1.08	-1.52	-10.84
1	-6.30	-1.68	-0.84	0.56	-8.26	-7.13	-6.31	-7.44	0.09	-0.50	-0.51	-0.83	-7.54
2	-3.42	-0.63	-0.20	0.02	-4.22	-4.00	-3.59	-4.22	0.01	-0.15	-0.13	-0.33	-4.15
4	-1.47	-0.16	-0.03	0.00	-1.66	-1.78	-1.62	-1.90	0.00	-0.02	0.01	-0.09	-1.80
8	-0.51	-0.03	0.00	0.00	-0.54	-0.64	-0.60	-0.69	0.00	0.00	0.02	-0.02	-0.65
12	-0.25	-0.01	0.00	0.00	-0.26	-0.33	-0.31	-0.36	0.00	0.00	0.02	0.00	-0.33

- a) Cornell *et al* force field, RESP HF/6-31G\* charges are used.
- b) Cieplak *et al* force field, RESP B3LYP/cc-pVTZ charges are used.
- c) Duan *et al* force field, RESP B3LYP/cc-pVTZ/ $\epsilon = 4.0$  charges are used
- d) polarization contribution including self-polarized dipoles
- e) polarization contribution without self-polarized dipoles

Table S7: DFT-SAPT and MM interaction energies for methylamine...methanol. Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM a)}}$	$E_{\text{elst}}^{\text{MM b)}}$	$E_{\text{elst}}^{\text{MM c)}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{ind}}^{\text{MMd)}$	$E_{\text{ind}}^{\text{MMe)}}$	$E_{\text{tot}}^{\text{MM a)}}$
-0.2	-25.28	-12.37	-8.62	39.81	-6.46	-12.14	-9.45	-11.59	10.12	-4.70	-1.97	-1.99	-6.72
0	-16.94	-7.05	-5.98	22.06	-7.91	-9.14	-7.12	-8.73	4.44	-3.21	-1.09	-1.10	-7.91
0.2	-11.57	-4.09	-4.19	12.12	-7.73	-7.00	-5.46	-6.70	2.06	-2.25	-0.64	-0.64	-7.19
0.5	-6.87	-1.87	-2.50	4.87	-6.36	-4.84	-3.78	-4.64	0.71	-1.37	-0.32	-0.32	-5.50
1	-3.31	-0.57	-1.09	1.04	-3.94	-2.80	-2.20	-2.70	0.15	-0.65	-0.12	-0.12	-3.31
2	-1.13	-0.08	-0.25	0.05	-1.42	-1.14	-0.90	-1.11	0.01	-0.19	-0.02	-0.03	-1.32
4	-0.27	-0.01	-0.03	0.00	-0.30	-0.31	-0.25	-0.30	0.00	-0.03	0.00	0.00	-0.34
8	-0.04	0.00	0.00	0.00	-0.05	-0.06	-0.05	-0.06	0.00	0.00	0.00	0.00	-0.06
12	-0.01	0.00	0.00	0.00	-0.01	-0.02	-0.02	-0.02	0.00	0.00	0.00	0.00	-0.02

- a) Cornell *et al* force field, RESP HF/6-31G\* charges are used.
- b) Cieplak *et al* force field, RESP B3LYP/cc-pVTZ charges are used.
- c) Duan *et al* force field, RESP B3LYP/cc-pVTZ/ $\varepsilon = 4.0$  charges are used
- d) polarization contribution including self-polarized dipoles
- e) polarization contribution without self-polarized dipoles

Table S8: DFT-SAPT and MM interaction energies for  $\text{Na}^+ \dots \text{Cl}^-$  Interaction energies in kcal/mol.

$r - R_0 [\text{\AA}]$	$E_{\text{elst}}^{\text{SAPT}}$	$E_{\text{ind}}^{\text{SAPT}}$	$E_{\text{disp}}^{\text{SAPT}}$	$E_{\text{exch}}^{\text{SAPT}}$	$E_{\text{tot}}^{\text{SAPT}}$	$E_{\text{elst}}^{\text{MM}}$	$E_{\text{exch}}^{\text{MM}}$	$E_{\text{disp}}^{\text{MM}}$	$E_{\text{ind}}^{\text{MM}}$	$E_{\text{tot}}^{\text{MM}}$
-0.5	-197.61	-18.18	-2.99	124.50	-94.29	-174.76	333.94	-4.72	-54.13	154.46
-0.4	-182.78	-16.42	-2.40	90.98	-110.62	-166.03	180.45	-3.47	-42.51	10.96
-0.3	-170.59	-15.04	-1.94	66.76	-120.82	-158.12	100.48	-2.59	-34.02	-60.23
-0.2	-160.31	-13.94	-1.58	49.15	-126.68	-150.93	57.50	-1.96	-27.64	-95.39
-0.1	-151.49	-13.06	-1.30	36.29	-129.56	-144.37	33.73	-1.50	-22.75	-112.14
0	-143.86	-12.31	-1.08	26.89	-130.36	-138.36	20.24	-1.16	-18.93	-119.28
0.1	-137.21	-11.65	-0.90	20.01	-129.74	-132.82	12.40	-0.91	-15.90	-121.33
0.2	-131.32	-11.02	-0.75	14.96	-128.12	-127.71	7.75	-0.72	-13.47	-120.69
0.3	-126.04	-10.41	-0.62	11.24	-125.84	-122.98	4.92	-0.57	-11.50	-118.63
0.5	-116.88	-9.25	-0.43	6.41	-120.15	-114.50	2.09	-0.37	-8.54	-112.78
0.7	-109.12	-8.13	-0.29	3.70	-113.84	-107.11	0.94	-0.25	-6.48	-106.43
1	-99.34	-6.57	-0.17	1.65	-104.43	-97.66	0.31	-0.14	-4.44	-97.50
1.5	-86.49	-4.37	-0.07	0.42	-90.51	-85.14	0.06	-0.06	-2.54	-85.14
2	-76.59	-2.81	-0.03	0.11	-79.32	-75.47	0.01	-0.03	-1.56	-75.48
3	-62.15	-1.11	-0.01	0.01	-63.26	-61.49	0.00	-0.01	-0.68	-61.50
5	-44.99	-0.19	0.00	0.00	-45.18	-44.87	0.00	0.00	-0.19	-44.87
10	-26.78	-0.02	0.00	0.00	-26.80	-26.78	0.00	0.00	-0.02	-26.78
15	-19.08	0.00	0.00	0.00	-19.09	-19.08	0.00	0.00	-0.01	-19.08
20	-14.82	0.00	0.00	0.00	-14.83	-14.82	0.00	0.00	0.00	-14.82

Note that values of the intermolecular interaction components are often numerically inaccurate at large separations and their ratios are therefore less reliable.