Supporting Information for Long–Range Electrostatic Corrections in Multipolar/Polarizable QM/MM Simulations

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1 LREC convergence tests

The calculations in this section were performed using the QM/MM system described in Section 5.1 of the main paper. All QM calculations were performed at the PBE0/6-31++G(d,p) level of theory.

1.1 Convergence with different exponents

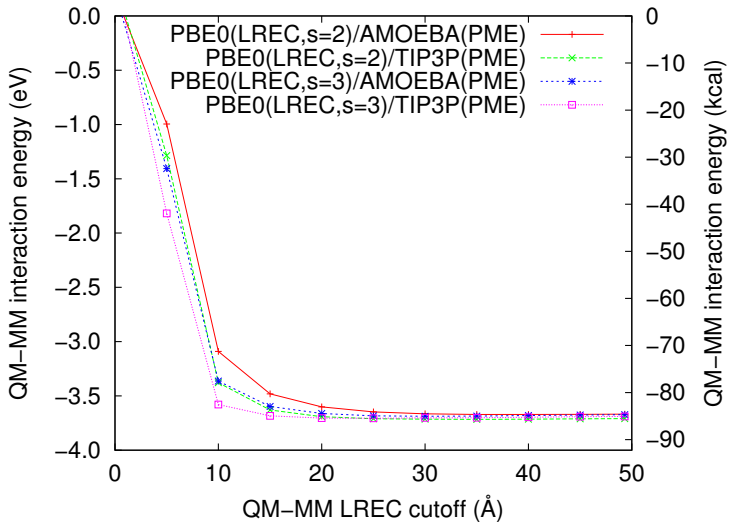

Figure 1: Convergence of PBE0(LREC)/MM(PME) calculations with different exponents and cutoff radii.

Fig. 1 reports the QM–MM interaction energy calculated using different LREC exponents and cutoff radii. Increasing the exponent from s=2 to s=3 accelerates the convergence of both monopolar and multipolar QM(LREC)/MM(PME) calculations and allows the user to decrease the cutoff by approximately 5 Å. Multipolar LREC calculations converge more slowly than the corresponding monopolar LREC calculations when the LREC exponents and number of atoms are equal. If the multipolar QM(LREC)/MM(PME) calculations employ a higher exponent than the monopolar QM(LREC)/MM(PME), then the two sets of QM/MM calculations can converge with the same cutoff radius (20-25 Å). In principle, the exponent could be adjusted to further reduce the cutoff radius and accelerate the QM part of the

calculations. However, a higher exponent and smaller cutoff radius could reintroduce the truncation artifacts that LRE methods are designed to remove.

1.2 Raw timings data

Table 1: Wall time for the PBE0(LREC)/MM(PME) calculations given in Figs. 5 and 6 in the main paper. All calculations were performed on an Intel Core i7 2.67 GHz workstation (8 threads) with LICHEM's NWChem/TINKER interface.

R_c (Å)	Wall time (hours)	
	TIP3P	AMOEBA
0.2500	0.0236	0.0308
5.0000	0.0238	0.0308
10.000	0.0244	0.0341
15.000	0.0258	0.0433
20.000	0.0288	0.0616
25.000	0.0341	0.0927
30.000	0.0416	0.1391
35.000	0.0522	0.2027
40.000	0.0666	0.2911
45.000	0.0847	0.3986
49.323	0.1041	0.5161

Table 1 reports the raw wall time (i.e. the total run time) for the QM(LREC)/MM(PME) calculations. In general, QM/MM calculations with the AMOEBA force field are more expensive than the corresponding TIP3P results. Additionally, the cost of the multipolar QM–QM and QM-MM portions of the calculations increases more rapidly compared to the monopolar results due to the larger number of one-electron integrals. Thus, increasing the exponent can result in a significant decrease in the wall time for QM/MM calculations, and has a larger effect on the efficiency of simulations employing multipolar force fields.