Electronic Supplementary Information:
Theoretical investigation of energy gap bowing in CdS_xSe_{1-x} alloy quantum dots

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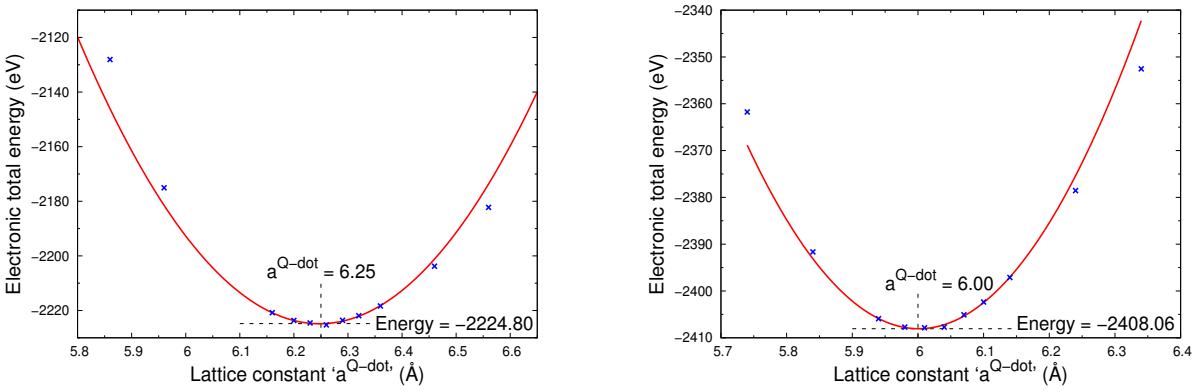
In order to estimate the effect of actual geometries of S atoms in the alloy QDs, we performed DFT calculations as shown in Table 1, for smaller sized (diameter 2 nm) alloy QDs, with ten different geometries generated by randomly substituting S atoms at Se sites, for the same value of $x = 0.15$ and $x = 0.79$. The values of the HOMO-LUMO gaps and the total energy are found to be same within the numerical accuracy of the calculations irrespective of the actual site occupation of the S atoms within the alloy QD. Total energy is found to be same within 0.5 % while the HOMO-LUMO gap is found to be same within 2 %. We have therefore concluded that if the CdS_xSe_{1-x} alloyed nanostructure is really homogeneous, then the single particle levels and the total energy are not crucially dependent on the actual geometric positions of the S or Se atoms but depend on the value of x.

Configuration No.	$x = 0.15$		$x = 0.79$	
	Total energy (eV)	HOMO-LUMO gap (eV)	Total energy (eV)	HOMO-LUMO gap (eV)
1	-590.077	2.072	-618.291	2.211
2	-590.098	2.070	-617.843	2.214
3	-590.638	2.068	-618.751	2.237
4	-590.617	2.071	-618.817	2.230
5	-590.112	2.068	-618.325	2.215
6	-590.558	2.089	-618.837	2.227
7	-591.239	2.061	-617.961	2.200
8	-591.770	2.063	-618.674	2.242
9	-591.200	2.062	-619.304	2.209
10	-591.151	2.086	-617.390	2.240

Table 1: Total electronic energy and HOMO-LUMO gap of CdS_xSe_{1-x} QD of size 2 nm for two different compositions $x = 0.15$ and $x = 0.79$ and for ten different geometric configurations.



(a) (b)

Figure 1: Variation of total electronic energy of passivated pure CdSe ($x = 0.0$) and CdS ($x = 1.0$) QDs of size 3.2 nm with different lattice constant a^{QD}.

size (nm)	HOMO-LUMO gap (eV) Our results	HOMO-LUMO gap[a] (eV)	HOMO-LUMO gap[b] (eV)	HOMO-LUMO gap[c] (eV)
1.9	–	–	2.85	–
2.0	–	2.88	–	2.79
2.2	2.981	–	–	–
2.3	–	2.73	–	–
2.4	2.797	2.68	2.47	
2.5	–	2.58	–	–
2.6	2.711	–	2.36	–
2.8	2.608	2.47	–	–
2.9	–	2.43	2.29	–
3.0	2.505	2.39	–	2.55
3.1	–	–	2.27	–
3.2	2.426	–	–	–
3.4	2.383	–	2.21	–
3.6	–	–	2.19	–
4.0	–	2.05	–	–
4.2	2.167	1.97	–	–
4.4	2.127	–	–	–
4.5	–	–	–	2.22
4.6	2.103	–	–	–

Table 2: Comparision of experimental and theoretical values of HOMO-LUMO gap for CdSe QDs: [a]ACS Nano, 2013, **7**, 4316, [b]ChemPhysChem, 2008, **9**, 2574, [c]Appl. Phys. Lett., 1999, **75**, 1751.

size (nm)	HOMO-LUMO gap (eV) Our results	HOMO-LUMO gap (eV) paper[a]	HOMO-LUMO gap (eV) paper[b]
2.2	3.471	–	–
2.3	–	3.17	–
2.4	3.291	–	–
2.5	–	3.11	–
2.6	3.211	–	–
2.75	–	–	3.13
2.8	3.114	–	–
2.9	–	3.04	–
3.0	3.020	–	–
3.1	–	3.1	–
3.2	2.946	–	–
3.4	2.905	–	–
3.7	–	2.81	–

Table 3: Comparision of experimental and theoretical values of HOMO-LUMO gap for CdS QDs: [a]ACS Applied Materials & Interfaces, 2012, **4**, 2561, [b]Journal of Luminescence, 2016,**171**, 79.

Size	HOMO-LUMO gap (eV)					
(nm)	$x = 0.00$	$x = 0.15$	$x = 0.36$	$x = 0.63$	$x = 0.79$	$x = 1.00$
2.20	2.981	2.999	3.103	3.205	3.295	3.471
2.40	2.797	2.827	2.920	3.031	3.079	3.291
2.60	2.711	2.738	2.830	2.942	3.011	3.211
2.80	2.608	2.634	2.729	2.855	2.918	3.114
3.00	2.505	2.539	2.628	2.761	2.816	3.020
3.20	2.426	2.469	2.549	2.666	2.751	2.946
3.40	2.383	2.422	2.520	2.630	2.707	2.905
4.20	2.167	2.206	2.307	2.424	2.509	2.713
4.40	2.127	2.168	2.258	2.377	2.469	2.649
4.60	2.103	2.138	2.246	2.363	2.458	2.655
bulk	1.740	1.804	1.916	2.099	2.227	2.420

Table 4: HOMO-LUMO gap for different sizes of QDs for various compositions x.

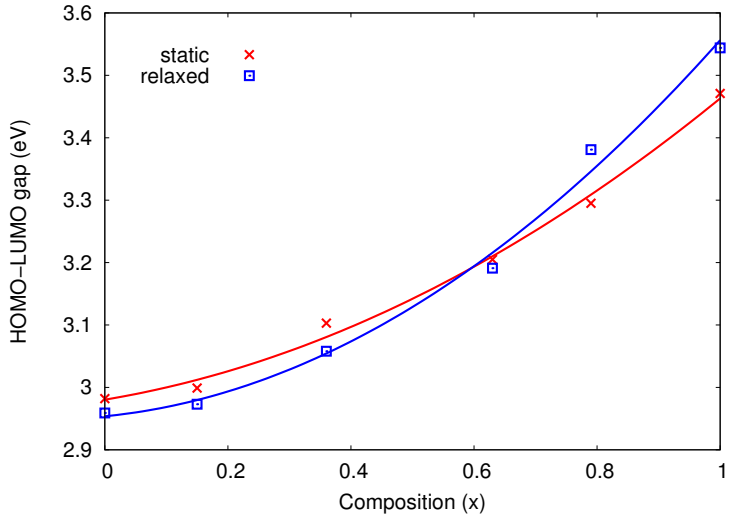


Figure 2: Comparision of values of HOMO-LUMO gap for static(red) and relaxed(blue) structures for six different composition x.

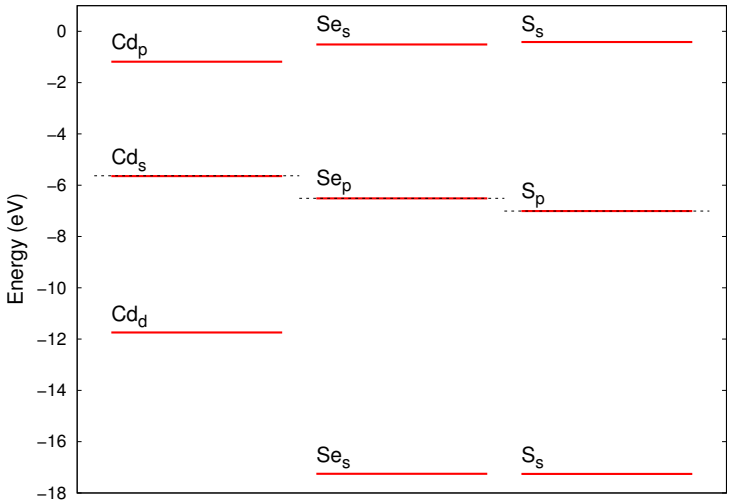
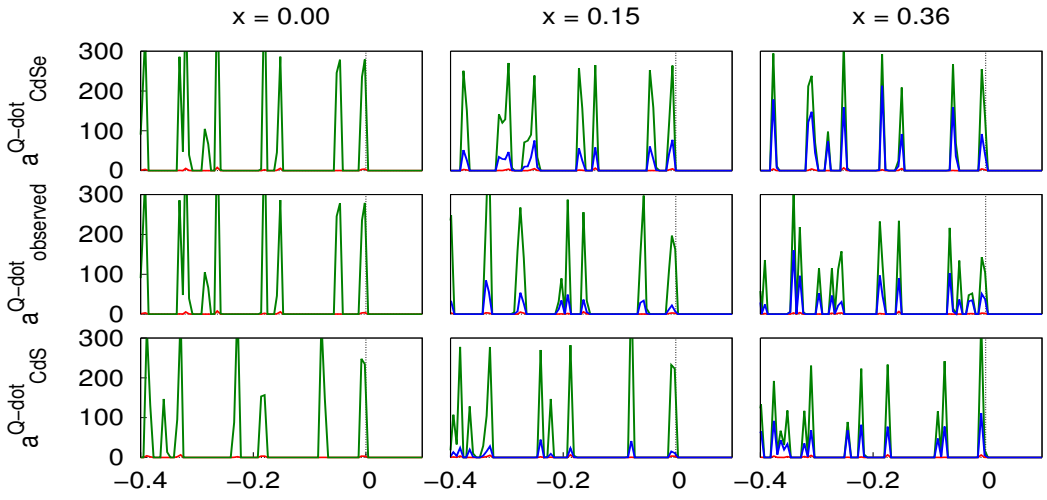
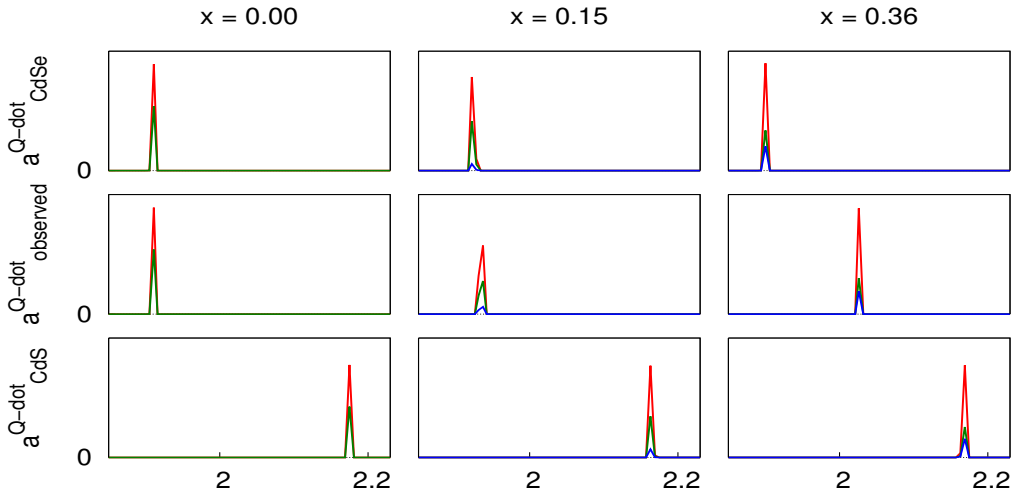


Figure 3: Energy level diagram for atomic systems Cd, Se and S. The black dotted line indicates the highest occupied level or valence energy level in the respective system. Valence energy level of Cd is close to valence energy level of Se than S valence energy level.

Figures 4 and 5 display site projected partial density of states (DOS) for states in the vicinity of HOMO and the LUMO states for six different compositions and three lattice constants used in our calculations. The energy difference between HOMO and (HOMO - 1) states decreases with an increase in lattice constant for all values of x. The contribution of the minority anion also increases in the vicinity of LUMO with an increase in lattice constant. The LUMO level shifts to higher energy value with a decrease in lattice constant, thus increasing the HOMO-LUMO gap with a decrease in lattice constant. For intermediate x values, the shift in LUMO increases with increase in S percentage. Moreover, the contribution of anion states decreases with an increase in lattice constant; the decrease being more for S than for Se states.

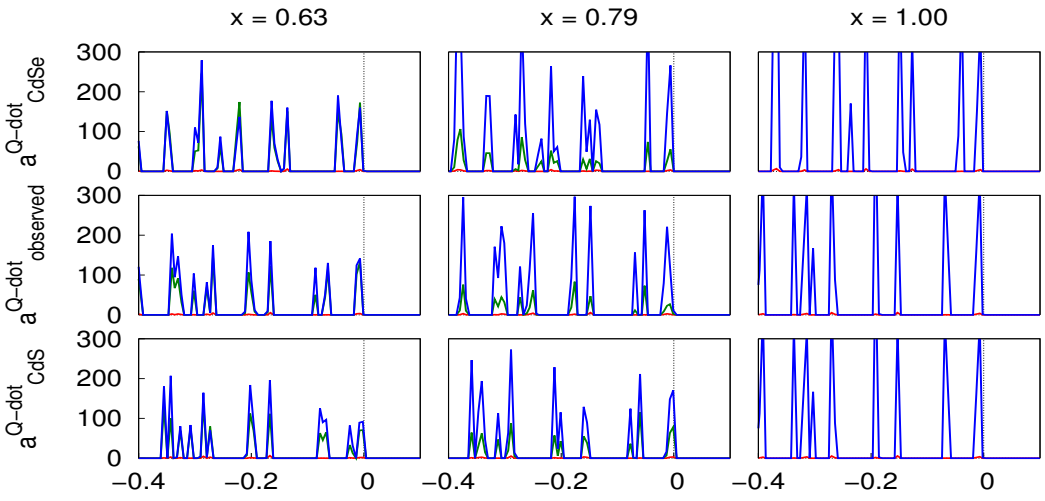


(a)

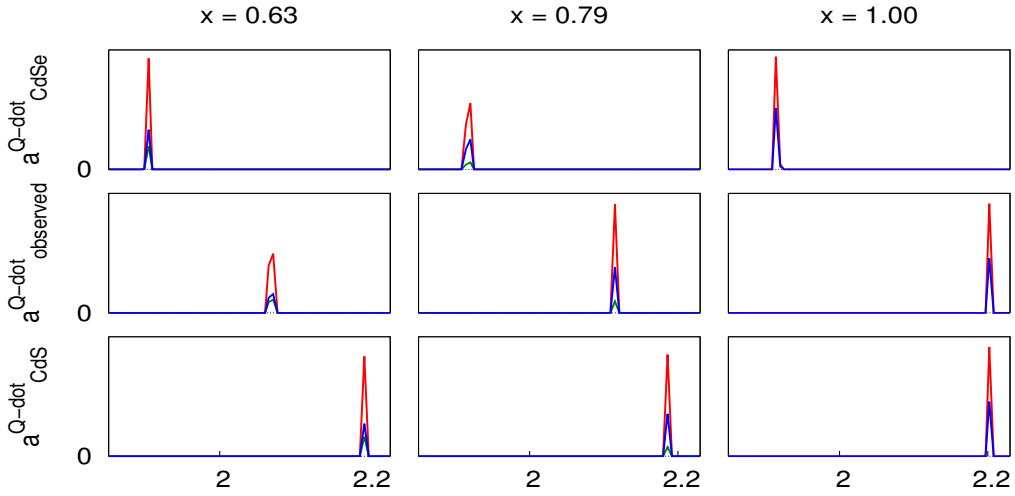


(b)

Figure 4: Site projected, ℓ-decomposed density of states for CdS_xSe_{1-x} QD of size 2.2 nm for $x = 0.00$ to $x = 0.36$ showing Cd s, Se p and S p states in red, green and blue respectively for states (a) near HOMO and (b) near LUMO for electronic structure calculations carried out for three different lattice constants.



(a)



(b)

Figure 5: Same as Fig. 4 for $x = 0.63$ to $x = 1.00$.

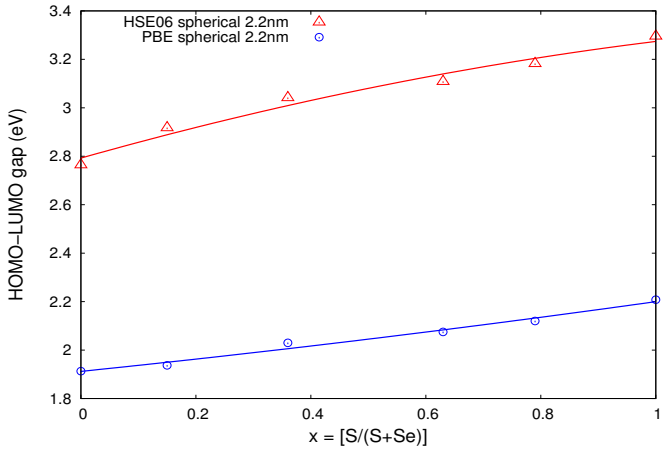


Figure 6: Variation of HSE06 and PBE energy gap (without bulk correction) for spherical QD of size 2.2 nm with composition x. Fitted quadratic equation for HSE06 and PBE are "$-0.188x^2 + 0.670x + 2.792$" and "$0.043x^2 + 0.244x + 1.912$". HSE06 bulk correction for CdSe and CdS are -0.25 eV and 0.15 eV respectively. PBE bulk correction for CdSe and CdS are 1.07 eV and 1.26 eV respectively.