SUPPORTING INFORMATION

The Effect of TiO_2 Morphology on the Electron Injection Efficiency in PbS Quantum Dot Solar Cells: a First-Principles Study

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Table S1. Valence excitation spectra of the PbS QD models. Vertical excitation energy (in eV) and the corresponding oscillator strength (in a.u.) are reported, along with the composition of the excited states. Only monoexcitations with % > 10% are reported. Results obtained at B3LYP/LANL2DZ.

	# Excitation	E (eV)	f (a.u.)	Composition
QD1	1	3.1534	0.0000	51% H – L 20% H-1 – L+1 15% H-2 – L +2
	2	3.1548	0.0000	42% H-2 – L+1 33% H-1 – L+2 13% H – L+2
	3	3.1850	0.0000	25% H-1 – L 24% H-1 – L+1 24% H – L 21% H – L+1
	4	3.1861	0.0000	44% H-2 – L 22% H – L+2 20% H-1 – L+2
	5	3.1866	0.0000	42% H-2 – L+1 31% H-1 – L+2 19% H – L+2
	6	3.2507	0.0002	47% H-1 – L 40% H – L+1
	7	3.2517	0.0002	40% H-2 – L 37% H – L+2 13% H-1 – L+2
	8	3.2523	0.0002	44% H-2 – L+2 34% H-1 – L+1 15% H – L+1
	9	3.2728	0.0000	31% H-2 – L+2 15% H-1 – L 15% H-1 – L+1 13% H – L
	10	3.9127	0.0000	59% H-3 – L+2 12% H-4 – L

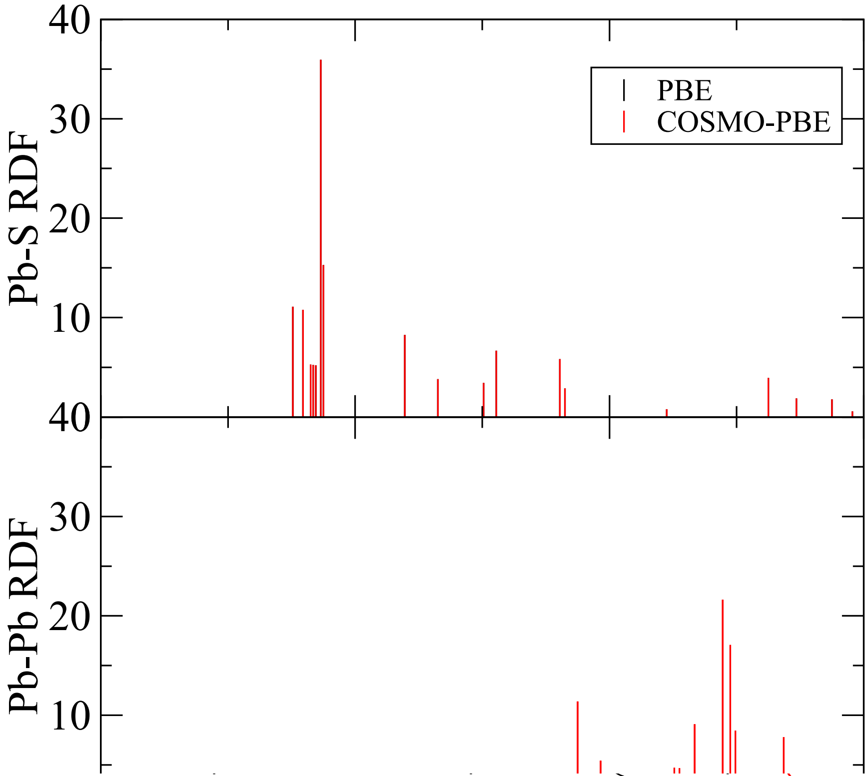
	# Excitation	E (eV)	f (a.u.)	Composition
QD2	1	2.45943	0.0118	99% H - L
	2	2.46143	0.0116	98% H-1 – L
	3	2.46253	0.0118	98% H-2 – L
	4	2.81978	0.0000	96% H-3 – L
	5	2.84798	0.0061	89% H-4 – L
	6	2.84928	0.0061	90% H-5 – L
	7	2.85148	0.0062	92% H-6 – L
	8	2.90229	0.0000	92% H-7 – L
	9	2.90469	0.0000	92% H-8 – L
	10	2.90999	0.0000	92% H-9 – L

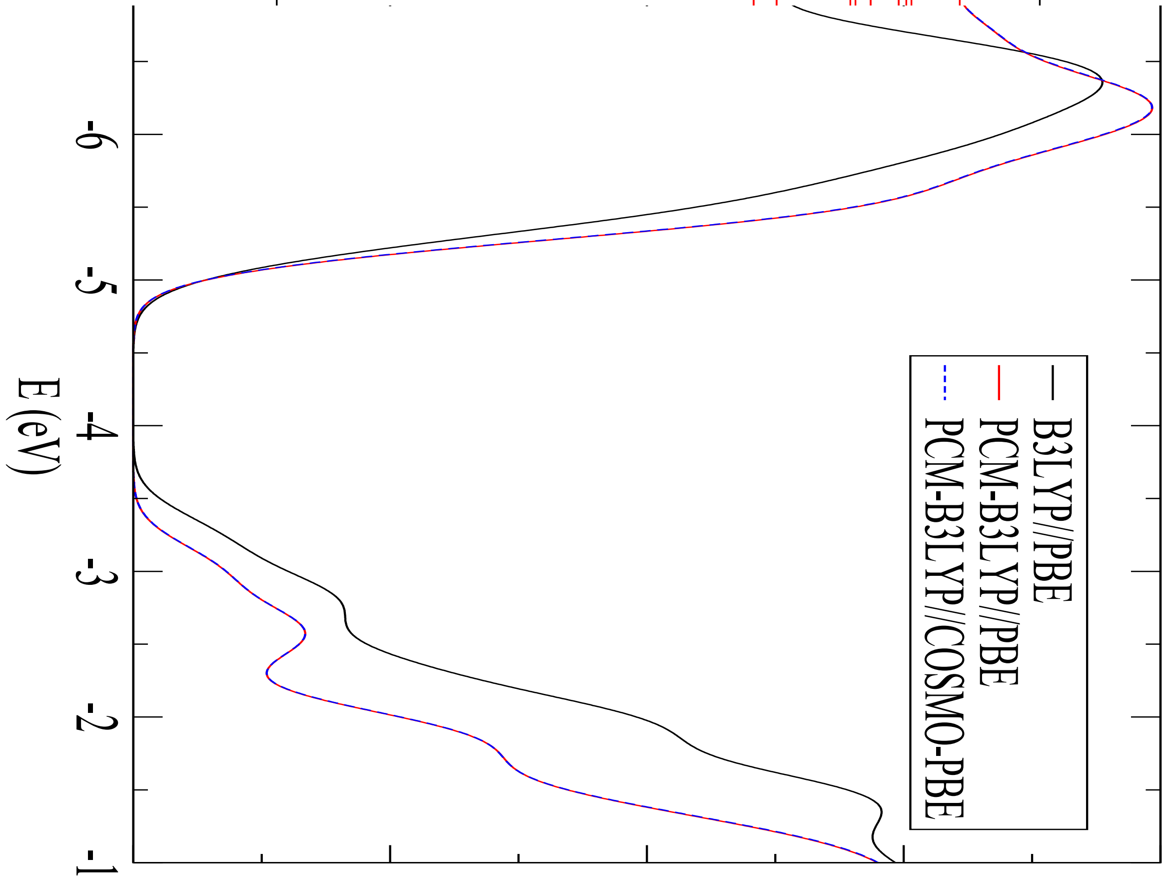
	# Excitation	E (eV)	f (a.u.)	Composition
QD3	1	2.14049	0.0011	97% H- L
	2	2.28391	0.0033	93% H-2 – L
	3	2.28891	0.0042	85% H-3 – L 10% H-1 – L
	4	2.29191	0.0004	89% H-1 – L 10% H-3 – L
	5	2.30051	0.0000	58% H-4 – L 38% H – L+1
	6	2.41182	0.0000	57% H – L+1 37% H-4 – L
	7	2.48643	0.0000	81% H-1 – L+1
	8	2.48723	0.0001	67% H-2 – L+1 23% H – L+2
	9	2.49424	0.0001	63% H-3 – L+1 24% H – L+3
	10	2.52204	0.0013	76% H-5 – L 19% H-4 – L

	# Excitation	E (eV)	f (a.u.)	Composition
QD4	1	1.95476	0.0002	37% H-5 – L 19% H-4 – L+1 11% H-2 – L
	2	1.95646	0.0002	32% H-3 – L+2 24% H-4 – L+1
	3	1.96906	0.0087	33% H-1 – L 31% H – L+1 12% H – L
	4	1.97056	0.0005	32% H – L 21% H-2 – L+1 13% H-4 – L
	5	1.97076	0.0057	18% H-1 – L 17% H-2 – L 16% H – L+1 12% H-2 – L+1
	6	1.97106	0.005	32% H-1 – L+1 19% H – L+2
	7	1.97237	0.0106	44% H – L+2 37% H-1 – L+1
	8	1.97437	0.0031	37% H-2 – L 18% H-2 – L+2 15% H – L+2
	9	1.97627	0.0049	36% H-1 – L+2 28% H-2 – L+2 10% H-4 – L+2
	10	2.01897	0.0	32% H-4 – L+1 17% H-3 – L+2 16% H-5 - L 13% H-3 L

	# Excitation	E (eV)	f (a.u.)	Composition
QD5	1	1.78574	0.0000	23% H-1 – L+1 18% H-2 – L 15% H – L 11% H – L+1 10% H-2 – L+2
	2	1.80504	0.0054	36% H-1 – L+1 22% H – L 16% H-2 – L
	3	1.80584	0.0056	24% H – L+2 23% H – L+1 20% H-2 – L
	4	1.80844	0.0057	37% H-2 – L+2 14% H-1 – L+2 12% H-3 – L+2
	5	1.88665	0.0000	17% H-1 – L 15% H-4 – L 13% H-2 – L+1 10% H – L+2
	6	1.88845	0.0000	16% H-1 – L+2 11% H - L
	7	1.91366	0.0003	18% H-1 – L 18% H-4 – L 15% H-5 – L 13% H-6 – L+1
	8	1.91596	0.0002	13% H-5 – L+1 11% H – L 10% H-6 – L+2
	9	1.91816	0.0004	18% H – L+2 11% H-6 – L+1
	10	1.91996	0.0033	24% H-2 –L+1 16% H-3 – L+1 15% H-1 – L

Figure S1. Pb-S, Pb-Pb, and S-S Radial Distribution Functions (RDFs) of QD5, calculated at the gas phase (black) and solvated (red) geometries.





Fi

States of QD5, calculated in *vacuo* (continuous black) and in the presence of implicit solvent (continuous red), on top of the gas phase geometry, and in the presence of implicit solvent (dashed blue), on top of the solvent geometry.

Figure S3. Simulated

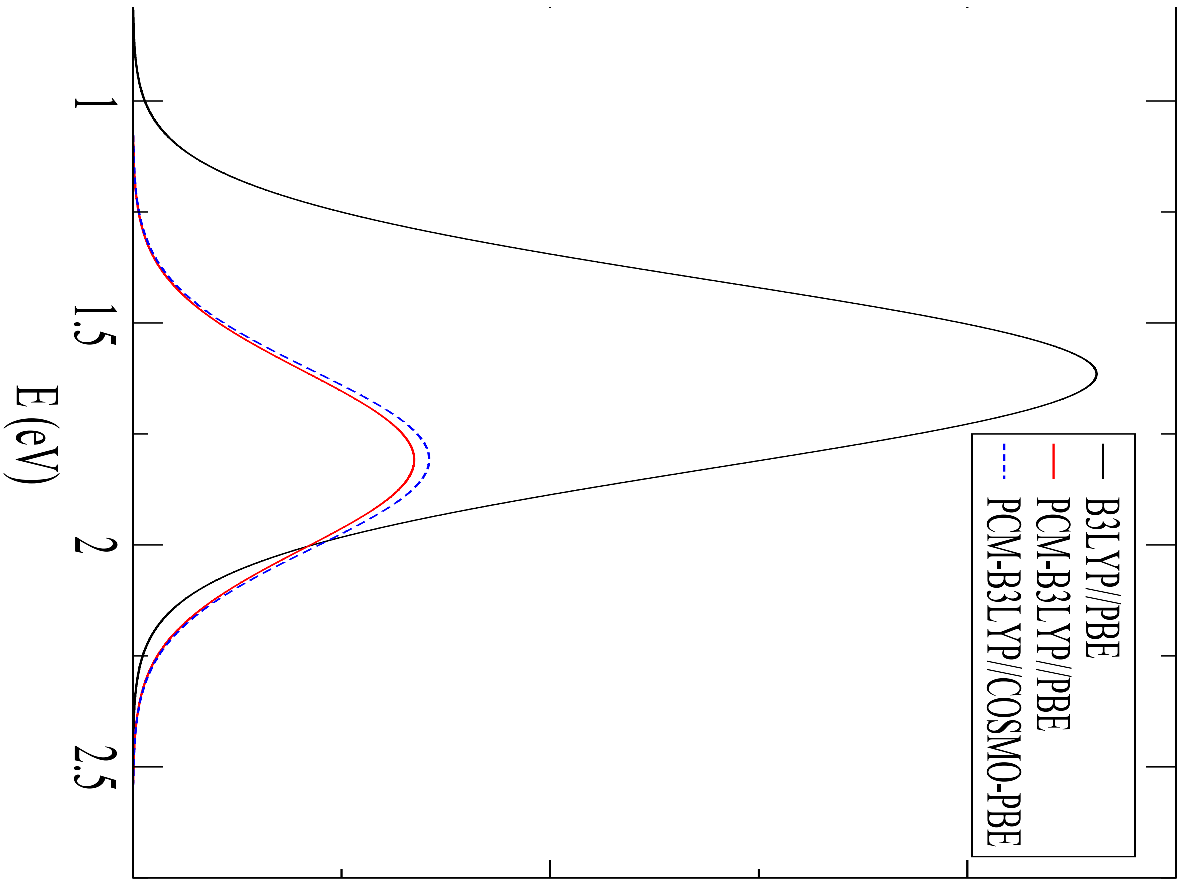


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Figure S4. Effect of the basis set size and the relativistic effects on the geometry of PbS QD models. Pb-S RDFs calculated on the geometries obtained by means of PBE and different basis sets.

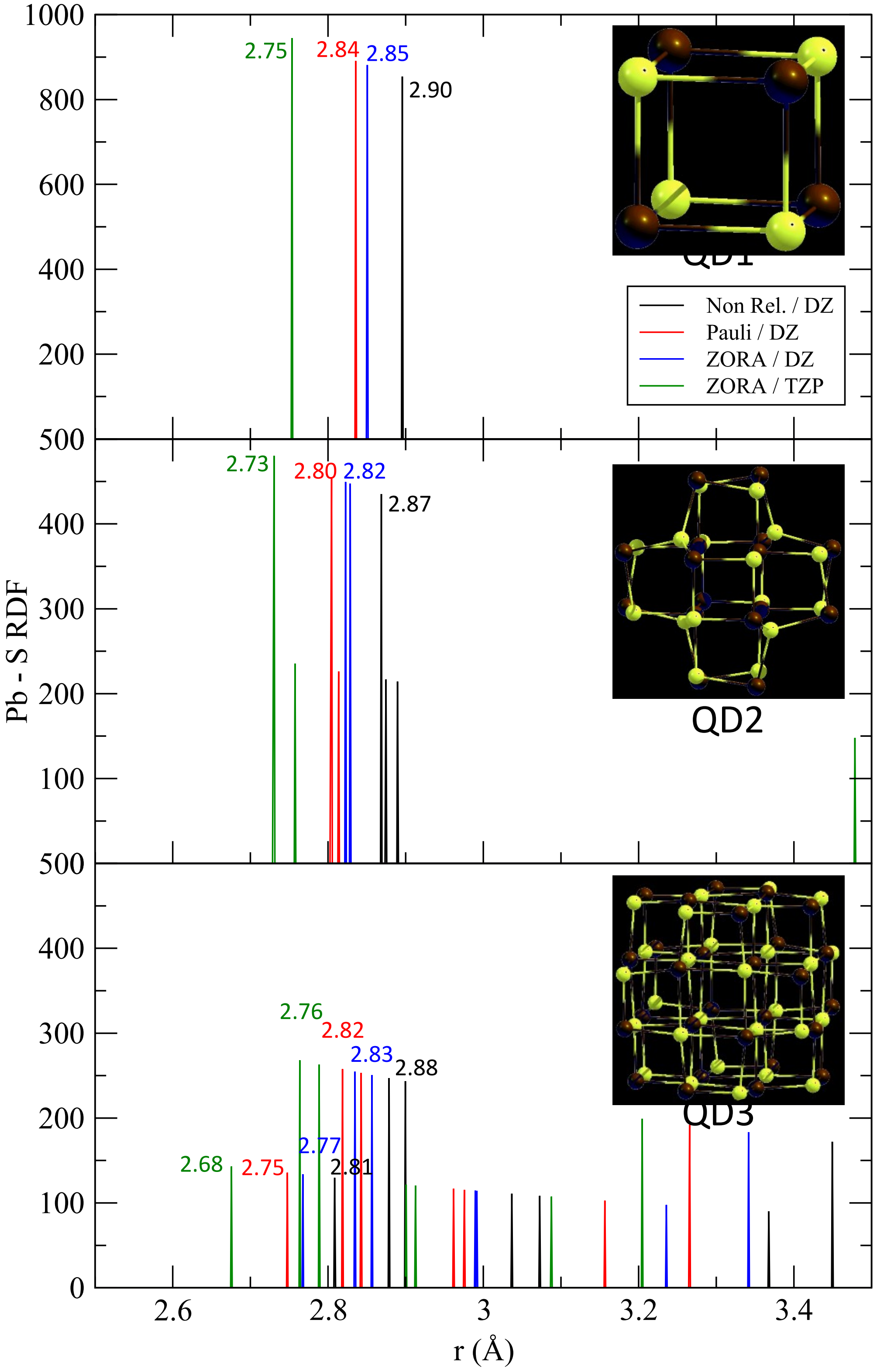
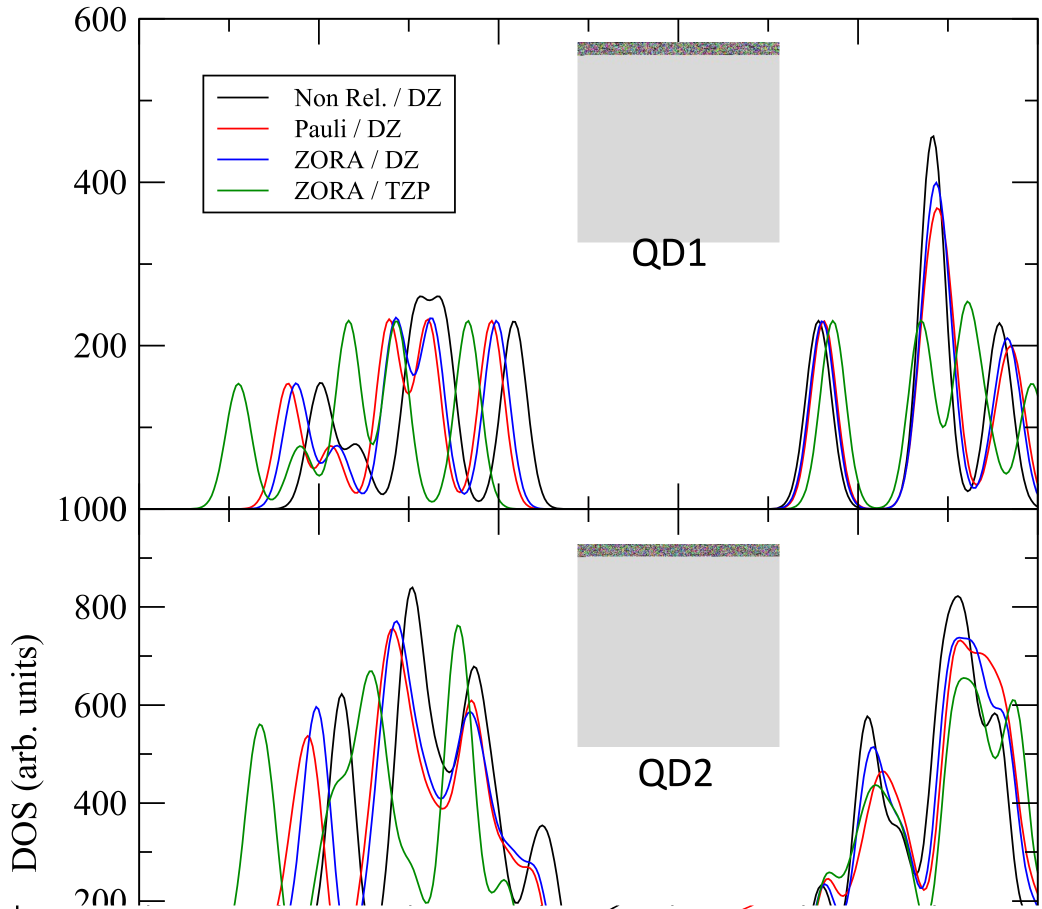
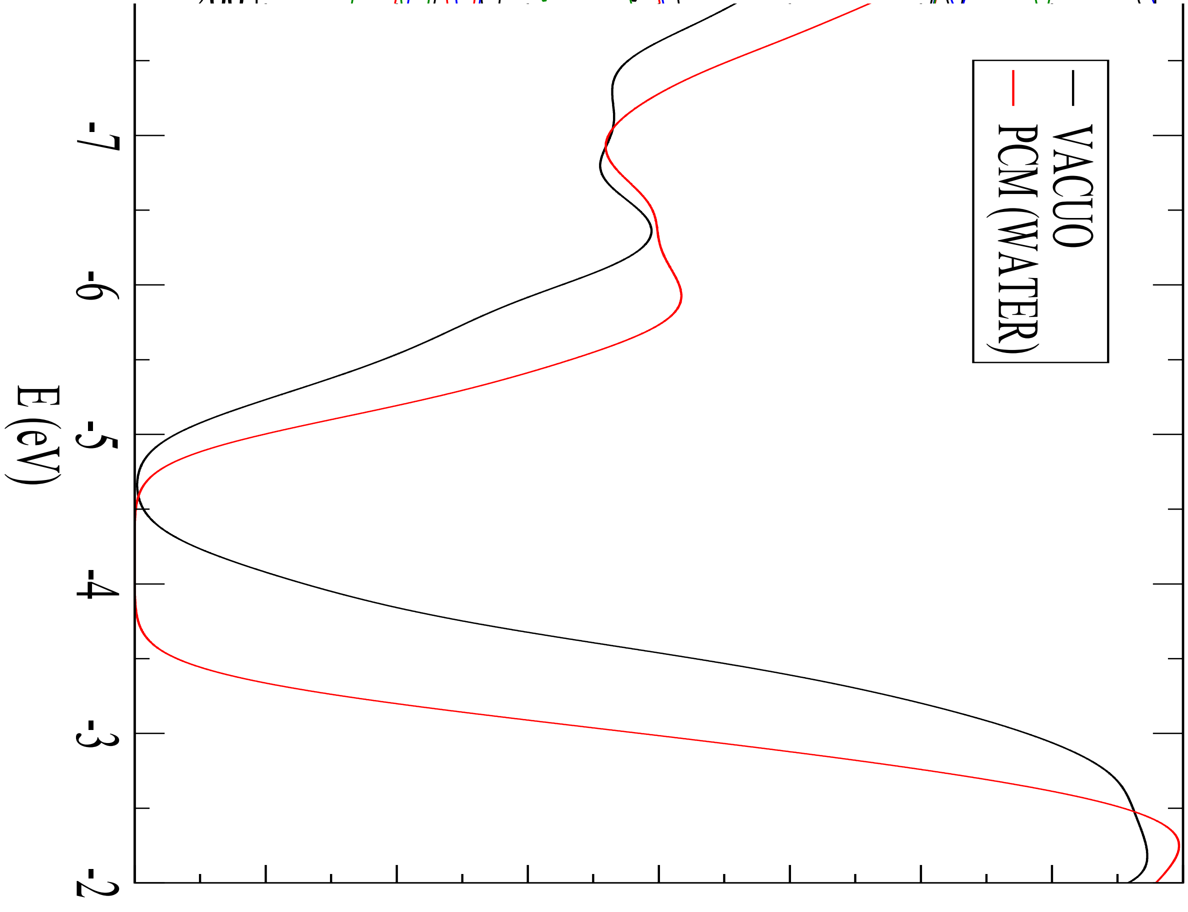


Figure S5. Effect of the basis set size and the relativistic effects on the electronic structure of PbS QD models. DOS calculated at B3LYP/LANL2DZ on top of the geometries obtained by means of PBE and different basis sets.


600
400
200
1000
800
600
400
200
DOS (arb. units)
Non Rel. / DZ
Pauli / DZ
ZORA / DZ
ZORA / TZP
QD1
QD2


-7
-6
-5
-4
-3
-2
E (eV)
VACUO
PCM (WATER)

presence of implicit solvent (red), calculated on top of the gas phase geometry.

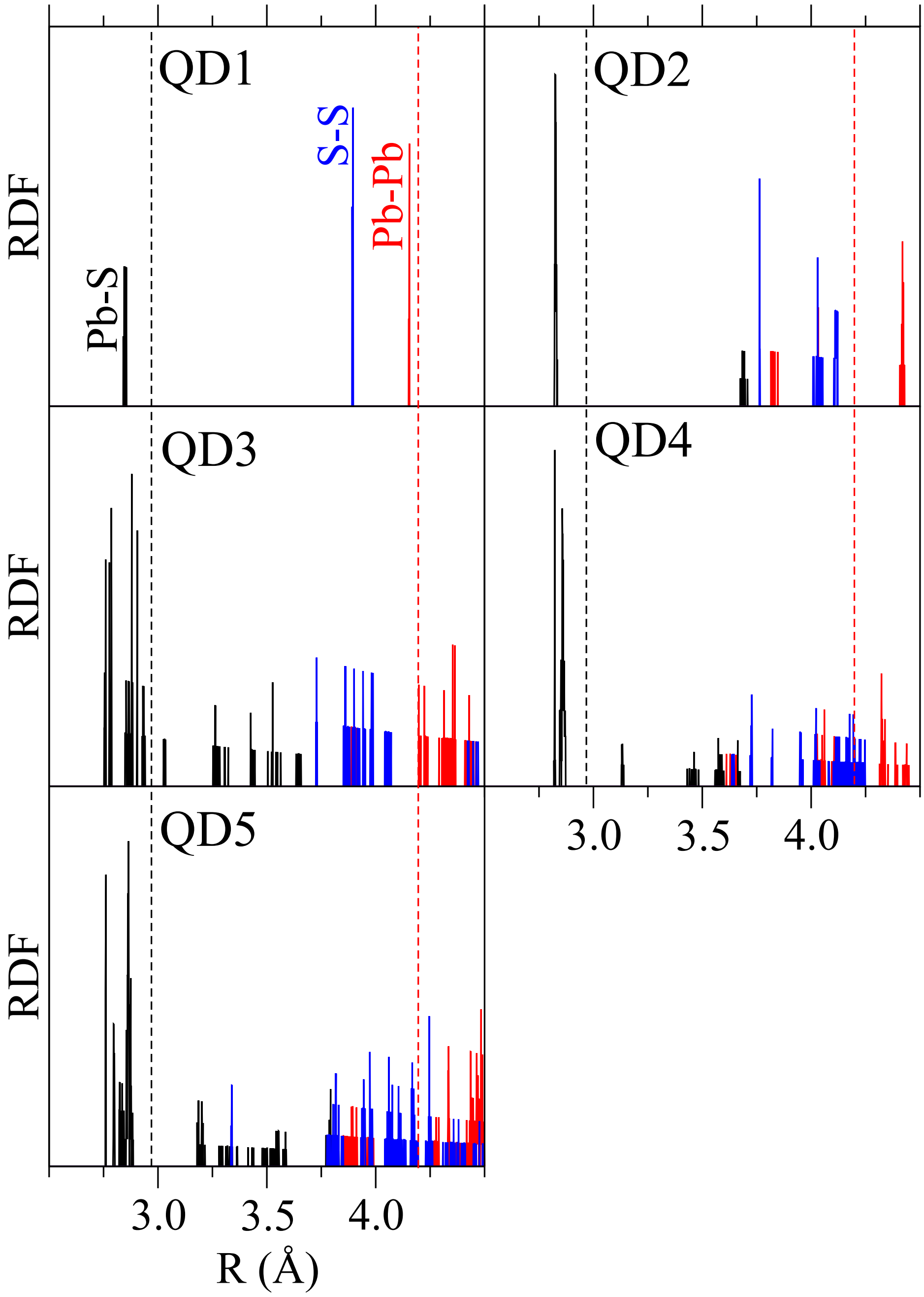
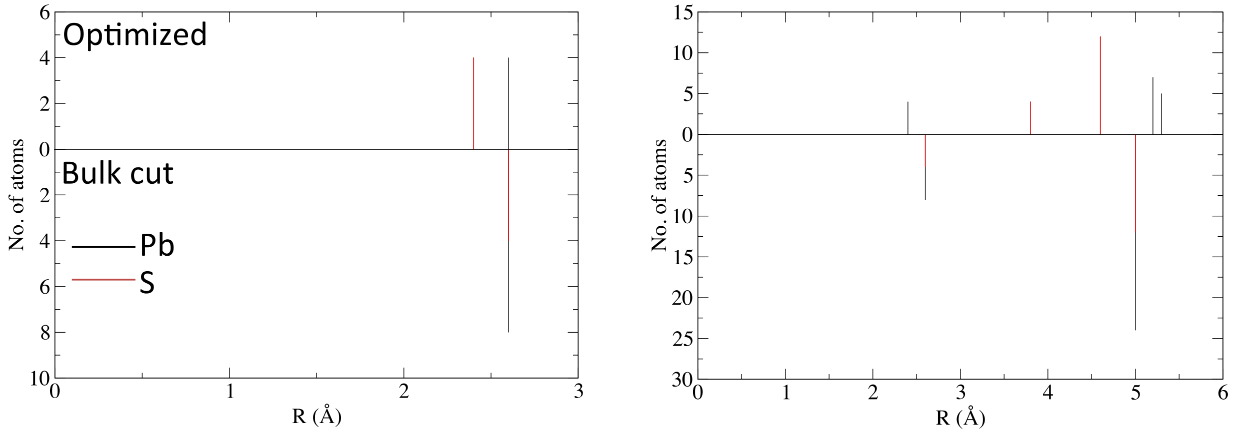


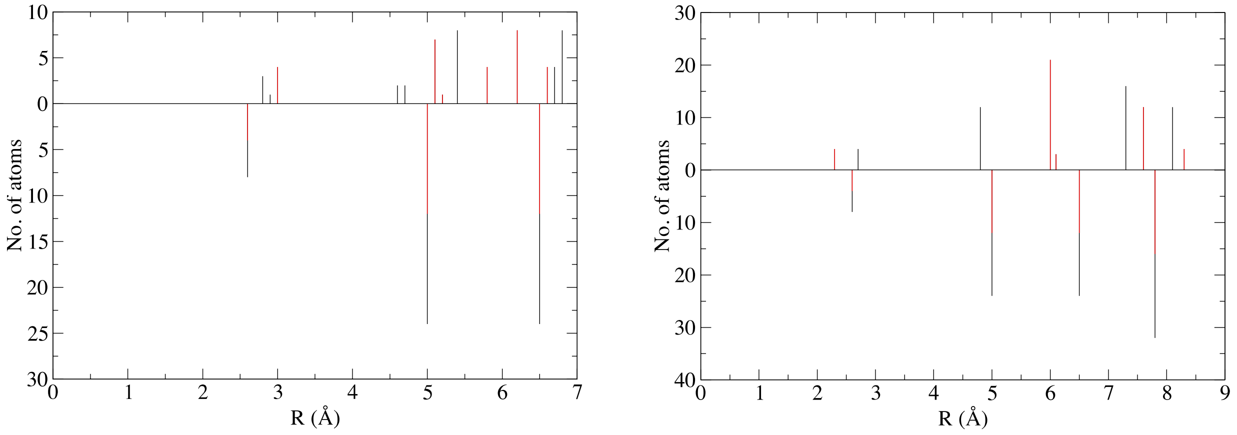
Figure S7. Pb-S (solid black), Pb-Pb (solid red), and S-S (solid blue) Radial

Distribution Functions (RDFs) of the PbS QD models studied. For comparison, the bulk Pb-S (dashed black) and Pb-Pb / S-S (dashed red) distances are also shown. Geometries obtained at the PBE/DZ level.

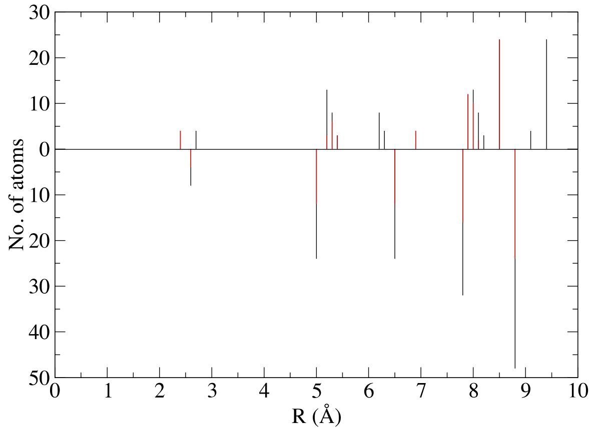
Figure S8. Radial Distribution Functions (RDFs) of the Pb (black) / S (red) atoms with respect to the center of the PbS QD models studied. The lower part of each panel shows the RDF of the QD model as cut from the bulk, whereas the upper part shows the RDF of the optimized QD. Geometries obtained at the PBE/DZ level.



(a) QD1 (b) QD2



(c) QD3 (d) QD4



(e) QD5

Figure S9. Average Pb-S
bond distance of each atom with
its neighbors as a function of
the radial distance of the
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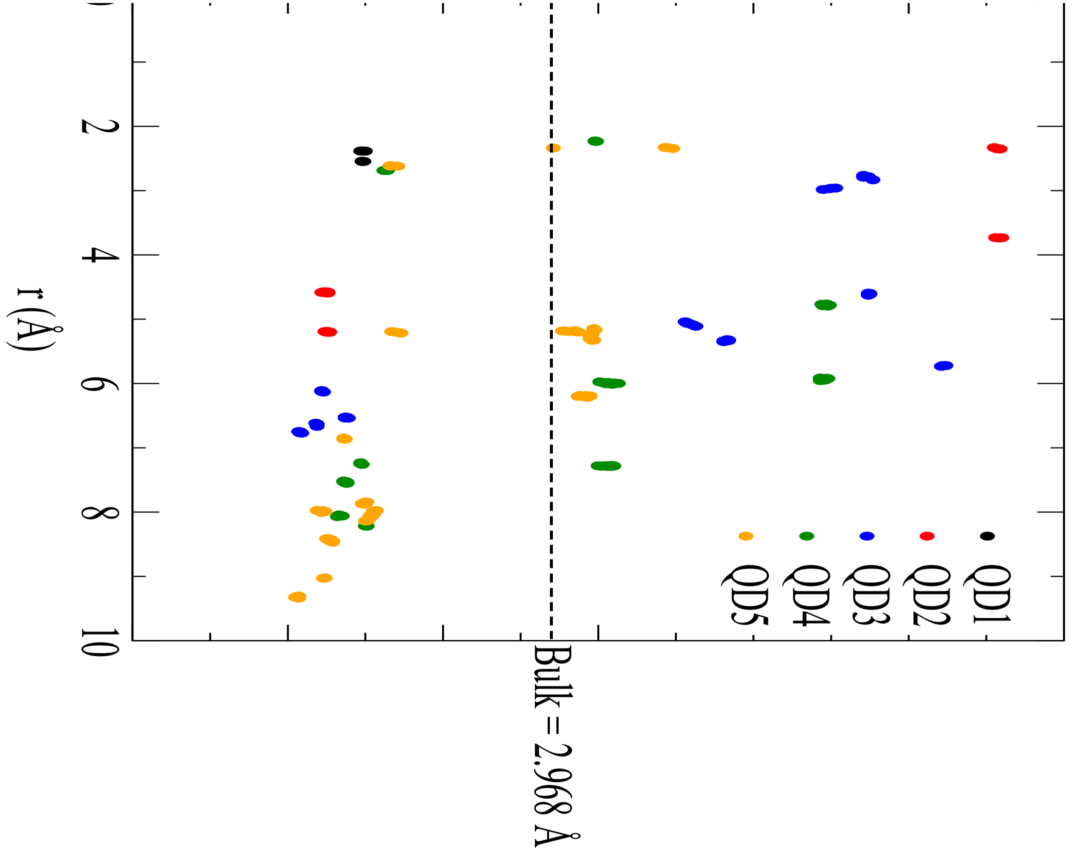

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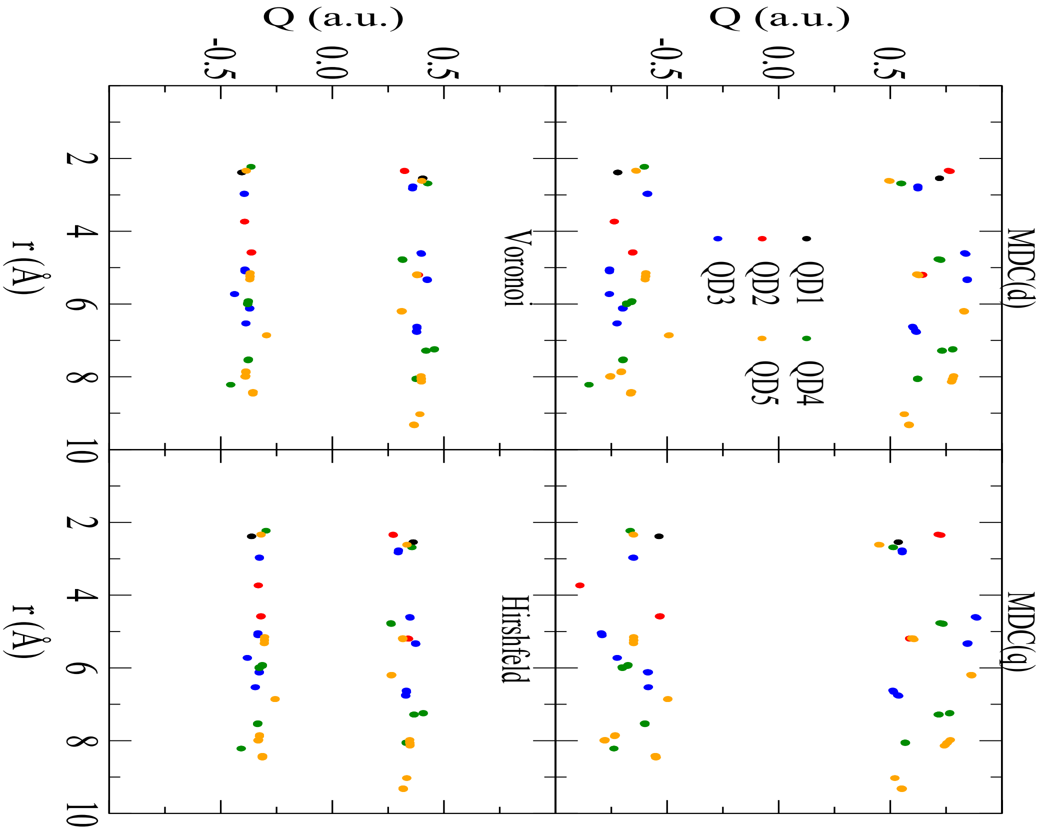
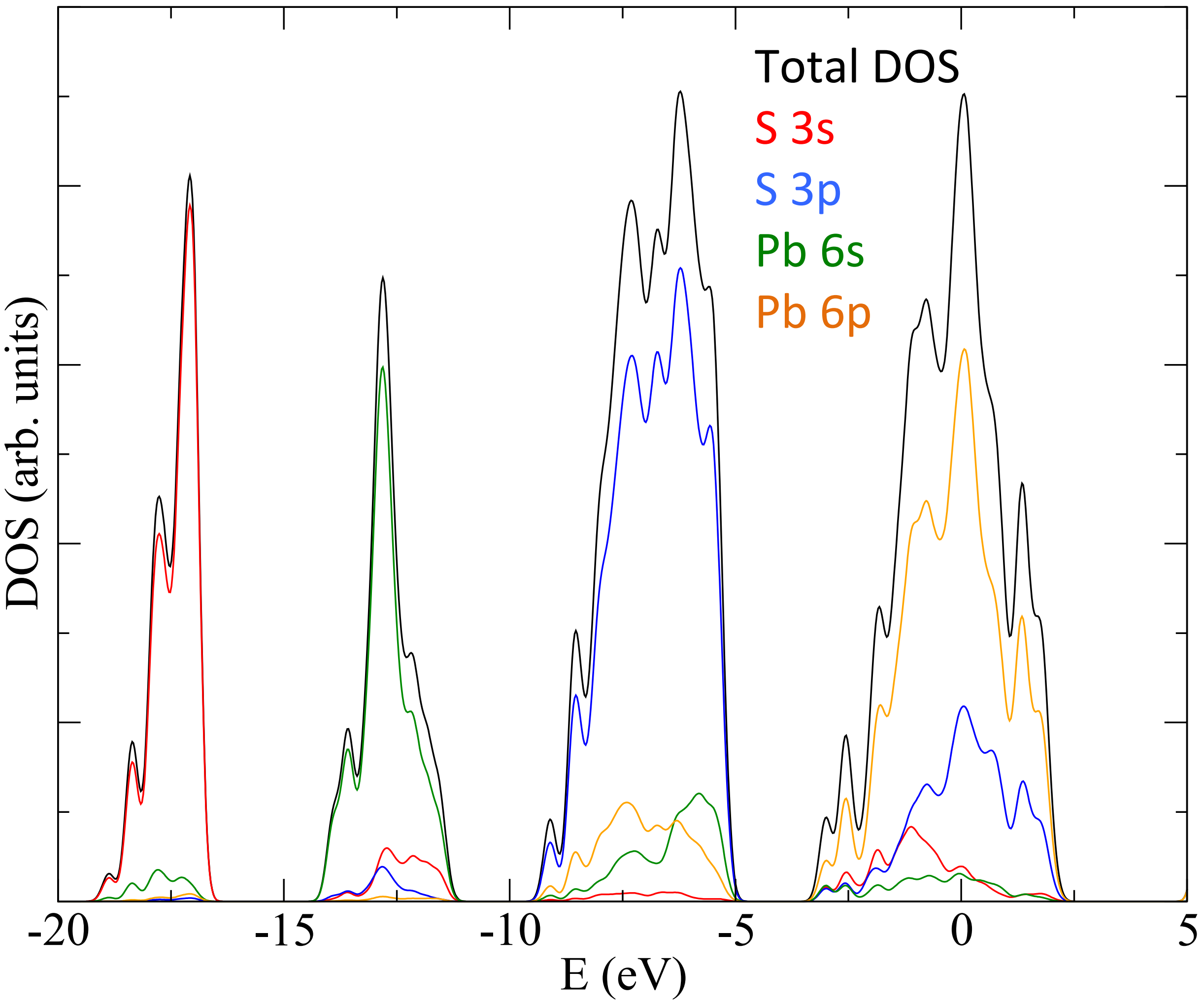


Figure S11. DOS of the QD5 model, obtained by a Gaussian convolution of $\sigma = 0.2$ eV of the individual orbitals, along with the projection into the atomic orbitals. Results obtained at the B3LYP/LANL2DZ level.


Total DOS
S 3s
S 3p
Pb 6s
Pb 6p
DOS (arb. units)
-20
-15
-10
-5
0
5
E (eV)