First-principles study of the electronic and optical properties of ZnO and ZnS wurtzite nanoclusters

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Abstract

Zinc oxide (ZnO) and zinc sulphide (ZnS) nanostructures have emerged in recent years as promising candidates in the development of nanoscale electronic and photonic devices. Theoretical studies on the properties of nanosized wurtzite ZnO and ZnS are rather scarce and their electronic and optical properties are largely unknown to date. As a part of a more general theoretical effort aimed at the multiscale modelling of nanohybrids for photovoltaics, we computed size-dependent electronic and optical properties of ZnO and ZnS nanoclusters with wurtzite structure, using Density Functional Theory (DFT), Time-Dependent DFT (TD-DFT) and Many Body Perturbation Theory methods. We discuss general trends for binding energy, ionization energy and electron affinity, fundamental electronic gap, excitonic effects, and optical absorption spectra as a function of cluster size and wire diameter. We found good agreement with the experimental data available for the two materials. A comparison between TD-DFT and Many Body theories shows for both materials a general good agreement for the optical absorption spectra of this class of nanocrystals.

1 Introduction

Since the discovery of fullerenes\(^1\) and carbon nanotubes\(^2\), the search for new nano-scaled materials based on elements other than carbon has received much attention. II-VI semiconductors attract intense interest in both nanoscale science and nanotechnology due to their unique electronic and optical properties. Zinc oxide (ZnO) and zinc sulphide (ZnS), in particular, are probably the most studied materials in the II-VI family owing to their main advantages: high abundance and stability, high transparency, large exciton binding energy, piezoelectricity, and biocompatibility\(^3\).

ZnO and ZnS share two types of crystal structures: hexagonal wurtzite and cubic zinc blende. There is an increasing interest in the non-centrosymmetric wurtzite structure, in which all Zn and O/S atoms are coordinated with four counter-ions. This gives rise to the existence of polar surfaces that, in turn, induce the formation of novel nanostructures. A large variety of ZnO and ZnS nanostructures with various morphologies (rods, wires, tubes, belts, ribbons, sheets, etc.)\(^4\text{–}^{10}\), as
well as ZnO-ZnS heterostructures\textsuperscript{11,12}, have indeed been synthesized. Due to quantum confinement effects, the chemical-physical properties of nanocrystals are sometimes superior for device applications when compared to those of bulk materials. These nanoscaled materials have therefore emerged as promising candidates in a wide number of applications, ranging from optoelectronics and gas-sensing, to catalysis and photovoltaics. In the field of photovoltaic energy production, in particular, ZnO is considered as a good alternative to TiO\textsubscript{2} in exciton solar cells, both in dye-sensitized\textsuperscript{13–16}, and quantum-dot sensitized\textsuperscript{17–19}. ZnO-nanocrystals / organic-polymer hybrid solar cells\textsuperscript{20–24} are a promising alternative to fully organic solar cells for future generation large-scale, cost-effective, flexible, and lightweight photovoltaic devices.

As a part of a more general theoretical effort aimed at the multiscale modelling of nanohybrids for photovoltaics\textsuperscript{25}, we computed size-dependent electronic and optical properties of ZnO and ZnS nanoclusters with wurtzite structures. While there have been a large number of theoretical studies devoted to ZnO\textsuperscript{26–38} and ZnS\textsuperscript{39–48} clusters, the electronic and optical properties of large ZnO and ZnS wurtzite nanocrystals are largely unknown to date.

The electronic ground-state of the nanocrystals here considered is described by density functional theory (DFT)\textsuperscript{49}. Thanks to the good compromise between accuracy and computational costs DFT has become the leading method for investigating ground-state properties of materials. It is well recognized, however, that the use of Kohn-Sham eigenvalues to determine the excited state properties of many-electrons systems yields, by and large, results in disagreement with experiments\textsuperscript{49}. For example, the well-known band-gap problem for bulk semiconductors arises from a severe underestimate (even exceeding 50\%) of the electronic excitation energies with respect to available experimental results (direct and inverse photoemission)\textsuperscript{50}. In optical absorption experiments, moreover, an electron excited into a conduction state interacts with the resulting hole in the previously occupied state and two-particles (excitonic) effects must be properly considered\textsuperscript{51}. For finite systems it is possible to obtain accurate electronic excitation energies using the so-called $\Delta$SCF approach\textsuperscript{49}. This method, successfully applied to several clusters (e.g., Si and Ge nanocrystals\textsuperscript{52}, C\textsubscript{60}\textsuperscript{53}), consists in evaluating total-energy differences between the self-consistent
field calculations performed for the neutral and charged systems (±1) to obtain the vertical electron affinities and first ionization energies. Based on the calculation of the total energies for the systems with N and N±1 electrons, respectively we thus computed the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) fundamental gap.

Staying in the DFT framework, optical excited states are properly described for finite systems by the Time Dependent DFT approach (TD-DFT)\(^{54}\). To compute the optical excited-states and the photo-absorption spectra we used two different implementations of TD-DFT in the linear response regime: (i) a frequency-space implementation based on the linear combination of localized orbitals, which is limited to the low-energy part of the spectrum, for both families NC1 and NC2 considered; (ii) a real-time propagation scheme using a grid in real space, yielding the complete photo-absorption spectrum, only for the NC1 family. The difference between the fundamental HOMO-LUMO gap and the optical gap, i.e. the lowest optically active singlet-singlet TD-DFT excitation energy as given in scheme (i), enabled a rough estimate of the excitonic effects occurring in these systems. The good description provided by both ASCF and TD-DFT is confirmed by Many Body Perturbation Theory calculations performed for the smallest clusters for both electronic gap and optical spectra.

The paper is organized as follows. Section 2 reports some technical details of the calculations. The results we obtained are presented and discussed in Section 3. Our concluding remarks are reported in Section 4.

2 Computational details

2.1 DFT calculations

For both ZnO and ZnS we considered two families of nanocrystals, labeled as NC1 and NC2, with diameters $\Phi$ of about 0.5 and 1.0 nm, respectively, and increasing length $L$ along the [0001] direction from 0.2 to 1.8 nm for NC1 and from 0.2 to 1.0 nm for NC2. The smallest clusters of NC1 and NC2 are formed by 4 atomic layers and contain 12 and 48 atoms, respectively; in previous
studies\textsuperscript{29,30,33} these clusters are denoted as 4L-12A and 4L-48A. Larger clusters are generated by repeating the structures along the [0001] direction. The initial structures, directly cut out from wurtzite ZnO, of the largest NC1 and NC2 nanocrystals are shown in Figure 1.

![Figure 1: Left panel: top and side views of the largest NC1 nanocrystal Zn\textsubscript{30}O\textsubscript{30} (diameter $\Phi \sim 0.5$ nm, length $L \sim 1.8$ nm). Right panel: top and side views of the largest NC2 nanocrystal Zn\textsubscript{72}O\textsubscript{72} (diameter $\sim 1.0$ nm, length $L \sim 1.0$ nm).](image)

To obtain the ground-state optimized geometries we used the quantum chemistry program package TURBOMOLE\textsuperscript{55}. DFT calculations have been performed with the gradient-corrected BP86 exchange-correlation functional, a combination of the Becke’s 1988 exchange functional,\textsuperscript{56} and the Vosko-Wilk-Nusair\textsuperscript{57} and Perdew’s 1986\textsuperscript{58} correlation functionals.

We first considered ZnO and for each cluster we directly cut out the starting configuration from the geometry of the bulk ZnO wurtzite crystal ($a = 3.258$ Å, $c = 5.220$ Å, $u = 0.382$ Å\textsuperscript{59}). Based on previous results\textsuperscript{29,30,33}, this initial structure was expected to be quite far from the final minimum.
configuration. We therefore started with the relatively inexpensive Gaussian atomic orbital basis set of split valence plus polarization quality def2-SV(P)\(^60\). We then used the optimal geometries and the corresponding self-consistent-field solution obtained in the previous step to refine the optimization with the def2-TZVP basis\(^60\), a split valence triple–\(\zeta\) quality augmented with polarization functions\(^60\). Results obtained using the def2-TZVP basis at the DFT level are expected to be not too far from the basis set limit\(^60\). We indeed verified for the smallest cluster considered, Zn\(_6\)O\(_6\) and Zn\(_6\)S\(_6\), that structural parameters and energetics (ionization energy, electron affinity, Kohn-Sham and fundamental HOMO-LUMO energy gaps) are coincident to within 0.3 % and 0.7%, respectively, with those obtained using the larger def2-QZVP basis set. To assess the accuracy of the chosen combination functional/basis set BP86/def2-TZVP we compared our results with the extensive benchmark study performed by Sorkin et al. for a few small ZnO and ZnS clusters\(^61\). As shown in Table 1, our results compare fairly well with those obtained using the M05-2X density functional, an hybrid metafunctional which was found to be the best DFT method to reproduce relativistic-core coupled cluster calculations\(^62\). The accuracy of the method employed is further confirmed by the computed ionization energy and electron affinity of the diatomic ZnO molecule, 9.40, and 2.21 eV respectively, in good agreement with the corresponding experimental values of 9.34±0.02\(^63\) and 2.09±0.01\(^64\).

To speed up calculations we used in all cases the resolution of identity approximation for computing the electronic Coulomb interaction\(^65\). This approach is based on the expansion of molecular electron densities in atom-centered auxiliary basis sets leading to expressions involving three-center electron repulsion integrals; this usually leads to a more than tenfold speedup, compared to the conventional treatments based on four-center electron repulsion integrals, without sacrificing

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Zn(_2)O(_2)</th>
<th>Zn(_3)O(_3)</th>
<th>Zn(_4)O(_4)</th>
<th>Zn(_2)S(_2)</th>
<th>Zn(_3)S(_3)</th>
<th>Zn(_4)S(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>1.904</td>
<td>1.834</td>
<td>1.801</td>
<td>2.257</td>
<td>2.191</td>
<td>2.170</td>
</tr>
<tr>
<td>From Ref. 61</td>
<td>1.869</td>
<td>1.813</td>
<td>1.787</td>
<td>2.255</td>
<td>2.196</td>
<td>2.176</td>
</tr>
</tbody>
</table>

Table 1: Comparison between the BP/def2-TZVP bond distances (in Å) of small ZnO and ZnS clusters and those given in Ref. 61, as computed using the M05-2X density functional.
accuracy. In addition, we made use of the multipole accelerated resolution of identity approxima-
tion\textsuperscript{66} that partitions the Coulomb interaction into the near- and far-field part enabling even more efficient calculations. In each SCF cycle we required the energy to be converged within $10^{-7} \ E_H$ and the grid for numerical evaluation of the exchange-correlation operator was set to medium size (gridsize m\textsuperscript{4}\textsuperscript{67}). All geometries were relaxed until the maximum norm of the Cartesian gradients was smaller than $1\times10^{-3}$ atomic units.

Geometry optimizations of ZnS nanocrystals started from the configuration of the BP/def2-TZVP optimized ZnO cluster with the same number of atoms. At the optimized geometry of both ZnO and ZnS neutral clusters we evaluated via total-energy differences the vertical electron affinity (EA\textsubscript{v}) and the vertical ionization energy (IE\textsubscript{v}). This enabled the calculation of the correct DFT gap of the neutral systems; this quantity is usually referred to as the fundamental gap and is rigorously defined within the $\Delta$SCF scheme\textsuperscript{49} as:

$$E_{\text{gap}}^1 = \text{IE}_v - \text{EA}_v = E_{N+1} + E_{N-1} - 2E_N,$$

(E\textsubscript{N} being the total energy of the N-electron system. As an additional consistency check we used also the following approximate expression:\textsuperscript{68}

$$E_{\text{gap}}^2 = \varepsilon_{N+1}^i - \varepsilon_N^i,$$

where $\varepsilon_i^j$ is the $i^{th}$ Kohn-Sham eigenvalue of the $j$-electron system. The results obtained using Eq. (1) and Eq. (2) tend to coincide as the system gets larger and the orbitals more delocalized.

Switching to another computational scheme one could employ Many Body Perturbation Theory in the so-called Hedin’s GW approximation\textsuperscript{51,68,69}. This method, in which the quasiparticle energies are calculated from the self-energy operator of the system (given as the product of the Green’s function $G$ and the screened Coulomb interaction $W$), gives results in excellent agreement with the available experiments for many materials (see e.g.,\textsuperscript{70,71}). However, GW calculations become prohibitively expensive for complex systems with large numbers of atoms, such as the largest
ones studied here. We therefore validated our fundamental DFT gap by computing the $G_0W_0$ electronic gaps only for the smallest clusters Zn$_6$O$_6$ and Zn$_6$S$_6$ considered. We performed the Many Body calculations in the plane waves - pseudopotentials framework with the package YAMBO$^{72}$. The code relies on DFT eigenvalues and eigenfunctions calculated from previous ground-state calculations with QUANTUM-ESPRESSO$^{73}$. Semicore states are included in the norm conserving pseudopotential, and a cutoff of 190 Ryd has been used in the DFT plane waves calculation. A cell of 40 a.u. side has been used, and to ensure convergence on vacuum, a Coulomb cutoff has been applied$^{78}$ in the many body calculations. The $G_0W_0$ calculations are done using the plasmon pole approximation. Gap values have been converged towards the number of plane waves, empty bands, and dimension of dielectric matrix whose inverse is used in the $W$ evaluation. A cutoff of 50 Ryd is used for both clusters, and 9000 plane waves are used for screening matrix inversion. The number of bands is 1000 for both systems, and all calculations are done at Gamma point.

### 2.2 TD-DFT and BSE calculations

To compute the excitation energies and electronic absorption spectra we used two different approaches within TD-DFT in the linear response regime, in conjunction with different representations of the wavefunctions:

1. the frequency-space implementation$^{79}$ based on the linear combination of localized orbitals, as given in the TURBOMOLE package$^{55}$

2. the real-time propagation scheme using a grid in real space$^{80}$, as implemented in the OCTOPUS computer program$^{81}$.

In the most widely used frequency-space TD-DFT implementation (1), based on the linear response of the density-matrix, the poles of the linear response function correspond to vertical excitation energies and the pole strengths to the corresponding oscillator strengths$^{82}$. With this method computational costs scale steeply with the number of required transitions and electronic excitations are thus usually limited to the low-energy part of the spectrum. The TD-DFT calculations
with TURBOMOLE were performed at the same level BP86/TZVP used to obtain the ground-state geometries and we restricted ourselves to the first few singlet-singlet electronic transitions.

In the second scheme (2) the time-dependent Kohn-Sham equations are directly solved in real time and the wavefunctions are represented by their discretized values on a uniform spatial grid. The static Kohn-Sham wavefunctions are perturbed by an impulsive electric field and propagated for a given finite time interval. In this way, all of the frequencies of the system are excited. The whole absolute photo-absorption cross-section $\sigma(E)$ is obtained from the dynamical polarizability $\alpha(E)$, which is related to the Fourier transform of the time-dependent dipole moment of the molecule through the equation:

$$\sigma(E) = \frac{8\pi^2 E}{hc} \Im\{\alpha(E)\},$$

(3)

where $h$ is Planck’s constant, $\Im\{\alpha(E)\}$ is the imaginary part of the dynamical polarizability, and $c$ is the velocity of light in vacuum. The dipole strength-function $S(E)$ is related to $\sigma(E)$ by the equation:

$$S(E) = \frac{m_e c}{\pi h e^2} \sigma(E),$$

(4)

$m_e$ and $e$ being respectively the mass and charge of the electron. $S(E)$ has units of oscillator strength per unit energy and satisfies the Thomas-Reiche-Kuhn dipole sum-rule $N_e = \int dE S(E)$, where $N_e$ is the total number of electrons. From a computational point of view the advantages of the real-time propagation method are discussed, e.g., in Ref. 83. On the other hand, the main drawbacks of the real-time approach are that: (i) no information is given on dipole-forbidden singlet-singlet and singlet-triplet transitions, and (ii) one does not obtain independent information for each excited state, such as its irreducible representation of the point group of the given system, and the description of the excitations in terms of promotion of electrons in an orbital picture.

We performed the OCTOPUS calculations in the local-density approximation (LDA), with the exchange-correlation energy density of the homogeneous electron gas\textsuperscript{84} parametrized by Perdew & Zunger.\textsuperscript{85} We verified for the smallest clusters that using the generalized gradient approximation with the parametrization of Becke\textsuperscript{56} and Perdew\textsuperscript{58} does not lead to significant changes over the
Table 2: Topological parameters for the NC1 and NC2 families of nanocrystals considered.

<table>
<thead>
<tr>
<th>Cluster (X = O, S)</th>
<th>(\Phi) (nm)</th>
<th>(L) (nm)</th>
<th>Number of atoms</th>
<th>(N_d)</th>
<th>2x</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Zn_6O_6)</td>
<td>0.5</td>
<td>0.2</td>
<td>0</td>
<td>6</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>(Zn_{12}O_{12})</td>
<td>0.5</td>
<td>0.6</td>
<td>0</td>
<td>18</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>(Zn_{18}O_{18})</td>
<td>0.5</td>
<td>1.0</td>
<td>0</td>
<td>30</td>
<td>6</td>
<td>42</td>
</tr>
<tr>
<td>(Zn_{24}O_{24})</td>
<td>0.5</td>
<td>1.4</td>
<td>0</td>
<td>42</td>
<td>6</td>
<td>54</td>
</tr>
<tr>
<td>(Zn_{30}O_{30})</td>
<td>0.5</td>
<td>1.8</td>
<td>0</td>
<td>54</td>
<td>6</td>
<td>66</td>
</tr>
<tr>
<td>(Zn_{24}S_{24})</td>
<td>1.0</td>
<td>0.2</td>
<td>12</td>
<td>24</td>
<td>12</td>
<td>48</td>
</tr>
<tr>
<td>(Zn_{48}S_{48})</td>
<td>1.0</td>
<td>0.6</td>
<td>36</td>
<td>48</td>
<td>12</td>
<td>72</td>
</tr>
<tr>
<td>(Zn_{72}S_{72})</td>
<td>1.0</td>
<td>1.0</td>
<td>60</td>
<td>72</td>
<td>12</td>
<td>96</td>
</tr>
</tbody>
</table>

chosen LDA. The ionic potentials are replaced by norm-conserving pseudo-potentials.\(^{86}\) In the real-space TD-DFT scheme the key parameters of the simulation are the grid-spacing and the radius of the sphere around each atom. From test calculations performed for the smallest cluster considered (\(Zn_6O_6\) and \(Zn_6S_6\)) we found that the total energy and the absorption spectrum converge using a uniform grid-spacing of 0.13 Å and a sphere radius of 5 Å. For the numerical integration of the time evolution we used a time step of 0.001 \(\hbar/eV\), which ensured energy conservation with good numerical accuracy, and propagated the wavefunctions for a time integration length \(T=20\ h/eV\ (\sim 0.7\ fs)\), corresponding to an energy resolution in the absorption spectra of \(\hbar/T=0.05\ eV\).

We validate our TD-DFT calculations by comparing them to results obtained with a higher level of theory. Using the \textsc{Yambo} code\(^{72}\) we thus performed optical calculations for \(Zn_6O_6\) and \(Zn_6S_6\) by directly solving the Bethe Salpeter equation (BSE) with a cutoff of 20 Ry, 3500 plane waves for local field effects, and by including the coupling term as described in Ref. 87. The electronic gap used in the BSE calculation is calculated in the \(G_0W_0\) framework described above.
3 Results and discussion

3.1 Ground-state properties

The size-dependent properties of the systems under investigation are presented and discussed as a function of the average number of dangling bonds per atom $\beta = N_d/2x$, $N_d$ and $x$ being the number of dangling bonds and the number of ZnO/ZnS dimers in the cluster, respectively. Obviously, the lower the $\beta$ value, the less the edge effect, being predominant the bulk behaviour in the limiting case of $\beta = 0$. Note that, while $2x$ its a measure of the volume of the system, the quantity $N_d$ is expected to be proportional to its surface. Given the cylindrical geometry of the systems under investigation, we thus expect $\beta \propto 1/\Phi$, where $\Phi$ is the diameter of the rod. As shown in Table 2 the two families considered, for which $\Phi_{NC2} = 2\Phi_{NC1}$, have the expected behaviour at increasing dimensions with $\beta$ values decreasing as $(2x+6)/2x$ up to 1, and $(x+24)/2x$ up to 0.5 for NC1 and NC2, respectively.

![Image](image.png)

Figure 2: Top and side views of the 20L-60A nanocrystals Zn$_{30}$O$_{30}$ (left) and Zn$_{30}$S$_{30}$ (right).

The ground-state optimized geometries of the largest NC1 and NC2 nanocrystals are shown in Figures 2-3; similar relaxed structures are found for the smaller clusters. The complete set of
Figure 3: Top and side views of the 12L-144A nanocrystals Zn$_{172}$O$_{72}$ (left) and Zn$_{172}$S$_{72}$ (right).

Cartesian coordinates for the nanocrystals considered are available in the Supplemetary Material.

As clearly seen from a comparison between Figure 1 and Figures 2-3, after geometry optimization all of the studied systems i) maintain an almost unchanged hexagonal cross-section along the [10\overline{1}0], and ii) loose completely the original conformation along the [0001] direction. A different behaviour, however, is observed for the four different families considered. More specifically, ZnO NC1, ZnO NC2 and ZnS NC1 appear to be shortened along the [0001] direction, a direct consequence of the merging of Zn-O and Zn-S double layers into single layers. This, in turn, gives rise to the formation of almost equilater parallelograms about 2.0Å side long, slightly distorted only at the top and bottom boundaries where side effects become dominant. Note that similar results have been already observed in previous studies for smaller ZnO wurtzite nanoclusters\textsuperscript{29,30,33}. As shown in Figure 3, a markedly different behaviour is found for ZnS NC2 nanocrystals, whose final minimum geometry is highly distorted along [0001] and can be viewed as composed by repeating units of 4L-48A clusters placed at the average distance of about 2.5 Å.

Overall, there are three remarkable features of the relaxed geometries: i) the bulk crystalline structure is generally maintained down to these nanoscale dimensions; ii) all systems reach a final
configuration with inversion symmetry and thus have no net dipole moment; iii) the surface Zn atoms relax towards the center by larger amounts than O/S atoms forming buckled Zn-O and Zn-S dimers, similarly to what has been found for the bare [10\bar{1}0] surface as well as for 1D infinite nanowires. This latter effect, in particular, is found to be more pronounced for the ZnS nanocrystals with buckling angles in the range 10-11° to be compared with angles of about 3-4° for ZnO nanocrystals. Note that the above points, combined with neutrality, stoichiometry and high coordination (all O/S atoms are coordinated with at least who Zn atoms, cf. Table 2) make these systems good cluster models for studying bulk and surface properties.

Table 3: Energies of the optimized ZnO and ZnS clusters of the NC1 family.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( \beta )</th>
<th>( E_{ch} )</th>
<th>IE</th>
<th>EA</th>
<th>( E^1_{gap} )</th>
<th>( E^2_{gap} )</th>
<th>HOMO</th>
<th>LUMO</th>
<th>( E^K_{gap} )</th>
<th>( E^{TD-DFT}_{opt} )</th>
<th>( E_{bind} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(_6)O(_6)</td>
<td>1.5000</td>
<td>-5.52</td>
<td>8.41</td>
<td>2.09</td>
<td>6.32</td>
<td>5.77</td>
<td>-6.06</td>
<td>-3.91</td>
<td>2.15</td>
<td>2.57</td>
<td>3.75</td>
</tr>
<tr>
<td>Zn(<em>{12})O(</em>{12})</td>
<td>1.2500</td>
<td>-5.94</td>
<td>7.67</td>
<td>1.61</td>
<td>6.06</td>
<td>5.65</td>
<td>-5.80</td>
<td>-3.83</td>
<td>1.97</td>
<td>2.02</td>
<td>4.04</td>
</tr>
<tr>
<td>Zn(<em>{18})O(</em>{18})</td>
<td>1.1661</td>
<td>-6.07</td>
<td>7.33</td>
<td>2.51</td>
<td>4.81</td>
<td>4.53</td>
<td>-5.74</td>
<td>-3.83</td>
<td>1.91</td>
<td>2.01</td>
<td>2.80</td>
</tr>
<tr>
<td>Zn(<em>{24})O(</em>{24})</td>
<td>1.1250</td>
<td>-6.13</td>
<td>7.12</td>
<td>2.40</td>
<td>4.72</td>
<td>4.49</td>
<td>-5.73</td>
<td>-3.82</td>
<td>1.91</td>
<td>1.92</td>
<td>2.80</td>
</tr>
<tr>
<td>Zn(<em>{30})O(</em>{30})</td>
<td>1.1000</td>
<td>-6.17</td>
<td>6.97</td>
<td>2.77</td>
<td>4.21</td>
<td>4.00</td>
<td>-5.71</td>
<td>-3.82</td>
<td>1.89</td>
<td>1.90</td>
<td>2.31</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( \beta )</th>
<th>( E_{ch} )</th>
<th>IE</th>
<th>EA</th>
<th>( E^1_{gap} )</th>
<th>( E^2_{gap} )</th>
<th>HOMO</th>
<th>LUMO</th>
<th>( E^K_{gap} )</th>
<th>( E^{TD-DFT}_{opt} )</th>
<th>( E_{bind} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(_6)S(_6)</td>
<td>1.5000</td>
<td>-3.28</td>
<td>8.19</td>
<td>1.93</td>
<td>6.26</td>
<td>5.94</td>
<td>-6.22</td>
<td>-3.58</td>
<td>2.64</td>
<td>2.90</td>
<td>3.36</td>
</tr>
<tr>
<td>Zn(<em>{12})S(</em>{12})</td>
<td>1.2500</td>
<td>-3.34</td>
<td>7.44</td>
<td>1.96</td>
<td>5.48</td>
<td>5.39</td>
<td>-5.89</td>
<td>-3.44</td>
<td>2.45</td>
<td>2.47</td>
<td>3.01</td>
</tr>
<tr>
<td>Zn(<em>{18})S(</em>{18})</td>
<td>1.1661</td>
<td>-3.41</td>
<td>7.32</td>
<td>2.33</td>
<td>4.99</td>
<td>4.82</td>
<td>-5.86</td>
<td>-3.63</td>
<td>2.24</td>
<td>2.54</td>
<td>2.45</td>
</tr>
<tr>
<td>Zn(<em>{24})S(</em>{24})</td>
<td>1.1250</td>
<td>-3.43</td>
<td>7.07</td>
<td>2.45</td>
<td>4.62</td>
<td>4.43</td>
<td>-5.87</td>
<td>-3.69</td>
<td>2.18</td>
<td>2.22</td>
<td>2.40</td>
</tr>
<tr>
<td>Zn(<em>{30})S(</em>{30})</td>
<td>1.1000</td>
<td>-3.44</td>
<td>6.90</td>
<td>2.66</td>
<td>4.24</td>
<td>4.22</td>
<td>-5.86</td>
<td>-3.71</td>
<td>2.15</td>
<td>2.18</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Table 4: Energies of the optimized ZnO and ZnS clusters of the NC2 family.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( \beta )</th>
<th>( E_{ch} )</th>
<th>IE</th>
<th>EA</th>
<th>( E^1_{gap} )</th>
<th>( E^2_{gap} )</th>
<th>HOMO</th>
<th>LUMO</th>
<th>( E^K_{gap} )</th>
<th>( E^{TD-DFT}_{opt} )</th>
<th>( E_{bind} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(<em>{24})O(</em>{24})</td>
<td>1.0000</td>
<td>-6.20</td>
<td>7.54</td>
<td>2.84</td>
<td>4.70</td>
<td>4.48</td>
<td>-6.08</td>
<td>-4.10</td>
<td>1.98</td>
<td>2.01</td>
<td>2.69</td>
</tr>
<tr>
<td>Zn(<em>{48})O(</em>{48})</td>
<td>0.7500</td>
<td>-6.39</td>
<td>7.10</td>
<td>3.18</td>
<td>3.93</td>
<td>3.85</td>
<td>-5.97</td>
<td>-4.24</td>
<td>1.73</td>
<td>1.76</td>
<td>2.17</td>
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<tr>
<td>Zn(<em>{72})O(</em>{72})</td>
<td>0.6666</td>
<td>-6.46</td>
<td>6.96</td>
<td>3.32</td>
<td>3.64</td>
<td>3.51</td>
<td>-5.90</td>
<td>-4.26</td>
<td>1.64</td>
<td>1.66</td>
<td>1.98</td>
</tr>
<tr>
<td>Zn(<em>{24})S(</em>{24})</td>
<td>1.0000</td>
<td>-3.69</td>
<td>7.63</td>
<td>2.20</td>
<td>5.43</td>
<td>5.18</td>
<td>-6.32</td>
<td>-3.27</td>
<td>3.05</td>
<td>3.23</td>
<td>2.20</td>
</tr>
<tr>
<td>Zn(<em>{48})S(</em>{48})</td>
<td>0.7500</td>
<td>-3.74</td>
<td>7.42</td>
<td>2.59</td>
<td>4.83</td>
<td>4.69</td>
<td>-6.39</td>
<td>-3.48</td>
<td>2.91</td>
<td>2.91</td>
<td>1.92</td>
</tr>
<tr>
<td>Zn(<em>{72})S(</em>{72})</td>
<td>0.6666</td>
<td>-3.76</td>
<td>7.18</td>
<td>2.79</td>
<td>4.39</td>
<td>4.37</td>
<td>-6.38</td>
<td>-3.57</td>
<td>2.81</td>
<td>2.82</td>
<td>1.57</td>
</tr>
</tbody>
</table>

From the total energy of the relaxed nanocrystals we computed the cohesive energy \( E_{ch} \), which gives a measure of the relative stability of the cluster. \( E_{ch} \) is computed as the difference between the total energy per dimer \( E_{av} \) and the sum of the total energies of isolated atomic Zn\(^{1}\)S) and O\(^{3}\)P)
or $S(^3P)$. One expects $E_{\text{ch}}$ to be reduced as compared to the corresponding bulk cohesive energy $E_{\text{ch}}^{\text{bulk}}$ by a quantity proportional to $\beta$ that can be defined as the energy per dimer $\sigma$ needed to create a dangling bond in the crystal:

$$E_{\text{ch}} = E_{\text{ch}}^{\text{bulk}} + \sigma \beta.$$  \hspace{1cm} (5)

Figure 4 displays the comparison between $E_{\text{ch}}$ for ZnO and Zns NC1 and NC2 nanocrystals, as a function of $\beta$. The computed cohesive energies, reported in Table 3 and Table 4, decrease at decreasing $\beta$, as expected from size effects. We found good correlation with linear regressions given by:

$$E_{\text{ch}}^{\text{ZnO}} = 1.61\beta - 7.94 \quad E_{\text{ch}}^{\text{ZnS}} = 0.39\beta - 3.86 \quad \text{for NC1},$$  \hspace{1cm} (6)

$$E_{\text{ch}}^{\text{ZnO}} = 0.77\beta - 6.97 \quad E_{\text{ch}}^{\text{ZnS}} = 0.20\beta - 3.89 \quad \text{for NC2}. \hspace{1cm} (7)$$

Figure 4: Cohesive energy of ZnO and ZnS nanocrystals of the NC1 (blue lines) and NC2 (red lines) family.
From the above equations, the limiting values corresponding to the bulk ($\beta = 0$) are about -7.0/-8.0 eV and -4.0 eV for ZnO and ZnS, respectively. These values are consistent with the bulk cohesive energies of the corresponding crystals, namely -7.5 eV for ZnO$^{93}$, and -3.2 for ZnS$^{94}$. By comparing Eq. (6)-Eq. (7) to Eq. (5) we find that the values of $\sigma$ corresponding to ZnO are about four times those found for ZnS. For both materials, in addition, we find that $\sigma_{NC1} \simeq 2\sigma_{NC2}$ which was also expected since $\sigma$ is by definition proportional to the inverse of the diameter $\Phi$.

### 3.2 Electronic properties

![Figure 5: Ionization energies (red) and electron affinities (blue) for ZnO (bottom) and ZnS (top) NC1 (right) and NC2 (left) nanocrystals, as a function of the topological parameter $\beta$.](image)

Our fundamental gaps of 6.32 and 6.26 eV for Zn$_6$O$_6$ and Zn$_6$S$_6$ calculated via total energy
Figure 6: Khon-Sham gap (red), exciton binding energy (violet) and DFT gap (blue) for ZnO (bottom) and Zns (top) NC1 (right) and NC2 (right) nanocrystals, as a function of the topological parameter $\beta$.

Differences (see Table 3 in Section 3) are in reasonable agreement with the corresponding $G_0W_0$ results of 6.9 and 6.6 eV, taking into account that the two methods usually give differences of some tenths of eV for clusters\textsuperscript{95–97}. We validate therefore the application of the $\Delta$SCF method to larger clusters for which $GW$ calculations are prohibitively expensive. The vertical ionization energies (IEs) and electron affinities (EAs) obtained via total energy differences are given in Table 3 and Table 4 and displayed in Figure 5 as a function of $\beta$. For NC1 nanocrystals we find for these quantities similar trends and limiting values (IE\textsubscript{ZnO} $\sim$ 7.0 eV, IE\textsubscript{ZnS} $\sim$ 6.9 eV, EA\textsubscript{ZnO} $\sim$ 2.8 eV, EA\textsubscript{ZnS} $\sim$ 2.7 eV). As a consequence, the limiting value of the fundamental DFT gap for NC1 nanocrystals of both compounds is roughly the same, about 4.2 eV. When going from NC1 to NC2,
the IEs of ZnO nanocrystals converge again to about 7.0 eV while their EAs are significantly larger, up to about 3.3 eV; the resulting ΔSCF gap is therefore smaller, about 3.6 eV, as expected due to a reduced quantum confinement. On the contrary, ZnS NC2 nanocrystals appear to converge to higher IEs (∼ 7.2 eV) and lower EAs (∼ 2.8 eV), which implies larger values of the fundamental DFT gap, about 4.4 eV. This result was not completely unexpected and can be seen as a direct consequence of the very different geometry of these clusters which break the symmetry along the [0001] direction, as compared to their ZnO counterparts (see Figure 3).

This markedly different behaviour of the ZnS NC2 nanocrystals is further testified by the computed DFT energy gaps and exciton binding energies. For each cluster considered, Table 3 and Table 4 compare the HOMO-LUMO gap $E_{KS}^{\text{gap}}$ obtained as difference of Kohn-Sham eigenvalues, the excitation energy of the HOMO-LUMO transition $E_{\text{TD-DFT}}^{\text{gap}}$ as given by frequency space TD-DFT, and the DFT gap computed via Eq. (1) and Eq. (2); the exciton binding energy $E_{\text{bind}}$ is estimated through the difference between $E_{\text{gap}}^1$ and the lowest optically active singlet-singlet TD-DFT excitation energy $E_{\text{opt}}^{\text{TD-DFT}}$. All of these quantities are displayed in Figure 6 as a function of $\beta$ and, as expected due to a reduction of quantum confinement effects, they all decrease as a function of molecular size. In particular, the HOMO-LUMO gap $E_{\text{gap}}^{KS}$ is found to decrease very slowly in all cases. However, while the HOMO and LUMO levels of ZnO and ZnS NC1 nanocrystals have similar energies and the gap for the latter is slightly larger than the one of the former (in the range 10-20%), the $E_{\text{gap}}^{KS}$ values for NC2 nanocrystals are very different with those of ZnS exceeding up to about 70% the corresponding values for ZnO. Interestingly, we found that $E_{\text{gap}}^{KS}$ and $E_{\text{gap}}^{\text{TD-DFT}}$ tend to coincide as the cluster size increases, a result already observed using for smaller ring-like and spheroidal ZnO clusters. As to the ΔSCF results, to the best of our knowledge the fundamental DFT gap has never been reported before for the nanocrystals considered. As expected from theoretical grounds we confirm that the values of $E_{\text{gap}}^1$ and $E_{\text{gap}}^2$ are indeed coincident at increasing cluster sizes. By comparing these values with the corresponding optical gap predicted by TD-DFT we could estimate the excitonic effects occurring in these systems. We found in all cases appreciable excitonic effects due to both quantum confinement and reduction of screening; $E_{\text{bind}}$ decreases...
in all cases and approaches the value of about 2 eV with the only exception of ZnO NC2 for which the exciton binding energy becomes as small as $\sim 1.6$ eV as a consequence of the largest optical gap of these clusters.

### 3.3 Photo-absorption spectra

![Absorption spectra comparison](image)

**Figure 7**: Comparison between the absorption spectra of Zn$_6$O$_6$ (top) and Zn$_6$S$_6$ (bottom) as obtained from BSE and TD-DFT. The BSE spectrum is in good quantitative agreement with the B3LYP spectrum reported in Ref. 48.

The absorption spectra of Zn$_6$O$_6$ and Zn$_6$S$_6$ from BSE and TD-DFT calculations are reported in Figure 7. The spectra display similar shapes, indicating that optical transitions are described in the same way by the two methods, TD-DFT and GW+BSE. The small shift is due to the inclusion of the GW gap opening in the MBPT calculations. Note that our BSE spectrum for Zn$_6$O$_6$ is in good quantitative agreement up to about 6 eV with the recent TD-DFT results reported in Ref. 48.
Figure 8: Absorption cross-section of ZnO (bottom) and ZnS (top) NC1 nanocrystals (Zn$_6$X$_6$ red, Zn$_{12}$X$_{12}$ blue, Zn$_{18}$X$_{18}$ violet, Zn$_{24}$X$_{24}$ cyan, and Zn$_{30}$X$_{30}$ yellow, X=O,S).

tained using the hybrid exchange-correlation functional B3LYP. From the analysis of excitonic energies and contributions, we find that for both materials the first two transitions (HOMO→LUMO and HOMO-1→LUMO) are optically dark, because they involve orbitals in the xy plane. The first optical active transition, at 2.57 eV with oscillator strength 0.030 for Zn$_6$O$_6$ and 2.90 eV with oscillator strength 0.016 for Zn$_6$S$_6$, is given by HOMO-2→LUMO states and is polarized along the z axis of the cluster. Excitonic binding energies, calculated from the MBPT with respect to the electronic GW gap, are 3.6 eV and 3.4 eV for Zn$_6$O$_6$ and Zn$_6$S$_6$, respectively, which compare fairly well with the estimates of 3.75 and 3.36 eV reported in Table 3. The good agreement found justifies thus the application of TD-DFT to larger systems with this kind of symmetry.

Figure 8 displays the absorption spectra of ZnO and ZnS NC1 nanocrystals as obtained through
the real-time real-space TD-DFT implementation of the OCTOPUS code. To ease the comparison, the spectra are normalized to the total number of dimers $2x$. Both compounds display a continuous redshift of the main peaks in the absorption spectrum at increasing sizes. This behaviour was expected as a consequence of the continuous decrease in the optical gap already observed from the frequency space TD-DFT results (cf. Table 3). In the case of ZnO NC1 nanocrystals, for the low-energy bands in the range 3.2-4.0 eV our results are consistent with those reported in Ref. 38.

4 Conclusions

We presented a systematic theoretical study of the size-dependent electronic and optical properties of ZnO and ZnS nanoclusters with wurtzite structures. We compared our results for two distinct families of nanocrystals, denoted as NC1 and NC2, with diameters of about 0.5 and 1.0 nm, respectively, and increasing length along the [0001] direction from 0.2 to 1.8 nm for NC1 and from 0.2 to 1.0 nm for NC2. The two families are found to differ from a topological point of view, quantified by the average number of dangling bonds per atom $\beta = N_d/2x$. Ground-state structural relaxations reveal common features for ZnO and ZnS NC1 and ZnO NC2 nanocrystals for which the starting bulk crystalline structure is maintained. ZnS NC2 nanocrystals on the contrary, while preserving the hexagonal cross-section, appear to be highly distorted along the [0001] direction. These structural changes are reflected in very different electronic and optical properties. From the ground-state structural relaxations performed at the BP/def2-TZVP level we computed cohesive energies, electron affinities, first ionization energies, and fundamental DFT gap in the framework of the $\Delta$SCF method. For the smallest clusters considered we found good agreement between $\Delta$SCF and $G_0W_0$ results, thus validating the application of this method to larger clusters. We computed also the photo-absorption spectra making use of the TD-DFT theoretical scheme. The systematic application of TD-DFT is justified by the close agreement found for the smallest systems with higher level BSE results. The two methods give the same description confirming the absence of charge transfer phenomena in these structures and the possibility of applying TD-DFT
to nanosystems that cannot be afforded by many body perturbation theory methods. In particular we used a compendium of the TD-DFT theoretical scheme in both frequency space, to obtain the optical gap and thus estimate the exciton binding energy, and real-time real-space, to obtain in a single step the whole absorption cross-section extending up to the far-UV. We remark that all of the free clusters considered satisfy general bonding principles such as neutrality, stoichiometry, balanced charge distribution, and coordination, which make them good cluster models for studying bulk and surface properties. The largest nanocrystals will be thus considered in conjunction with organic compounds to study the optoelectronic properties of hybrid interfaces.

**Acknowledgement**

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**Supporting Information Available**

Cartesian coordinates of the ZnO and ZnS nanocrystals considered. This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

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