Large-scale ab initio nanostructure electronic structure calculations for energy applications

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Abstract. Nanostructures have often been used to construct third-generation solar cells and for solid state lighting. To fully explore the potential for such energy applications, we need to understand the electronic and optical properties of the corresponding nanosystems. These include the quantum confinement effects, the electron hole separations, the exciton binding energy, and optical absorption spectrums. In the past ten years, we have developed a systematic approach to study such properties of thousand atom nanostructures based on ab initio calculations and large scale computations. In this paper, we present a few examples using such an approach to study the nanostructure properties related to energy applications.

1. Core/shell nanowire for solar cells
One of the challenges for massive solar cell deployment to solve the global energy crisis is to find cheap and abundant material. Unfortunately, the most abundant and environmentally benign semiconductors (e.g., the metallic oxides) all have band gaps too large for optimal solar cell application. One possibility is to stack two such large band gap materials together. If they have a type-II band alignment – which means one material’s valence band maximum (VBM) and conduction band minimum (CBM) are both higher than the other material’s VBM and CBM, respectively – then the overall band gap of the whole system will be reduced, thereby making it suitable for solar cell applications. Since the small band gap optical absorption happens only near the interface of these two materials, it is necessary to make such a device in nanoscale, so the interface area occupies a big proportion of the whole system.

We have studied ZnO/ZnS nanowires [1] using the charge patching method (CPM) [2] and direct density functional theory (DFT) calculations. In the nanowire, ZnO is the core, which is surrounded by a shell of ZnS. Both ZnO and ZnS are abundant and environmentally friendly materials. Moreover, these semiconductors are very stable. Although the band gaps of ZnO and ZnS are both larger than 3 eV, the combined system has a overall band gap of about 2 eV, which makes a theoretically possible solar cell efficiency of 23%. The absorption amplitude of the system close to the band gap is similar to that of bulk Si. Although this is not as strong as the direct band gap material, it nevertheless makes such systems feasible for solar cell applications. In figure 1, we show the geometry of the nanowire and its optical absorption spectrum. We see that there are strong absorption below the bulk ZnO and ZnS band gaps. In figure 2, we show the hole (VBM) and electron (CBM) wave functions. The electron wave function is localized in the core, while the hole wave function is localized in the shell. There is an advantage for such separation. In many solar cell devices using both inorganic nanocrystallines and organic polymers, the hole is conducted by the conjugated polymers. Thus, the
A hole localized at the outer shell can be readily transferred to polymers attached to the periphery of the wire.

2. A spherical core in a nanorod

Besides core/shell nanowires, we have studied other core shell structures. While spherical core/shell quantum dots have been synthesized for many semiconductor materials, recently, a nonsymmetric rod has been synthesized with one spherical core embedded in one end of the rod [3,4]. Such structure is interesting because it provides the opportunity to manipulate the electronic states through band alignment, elastic strain, surface dipole moment, and quantum confinement effect. Many of these factors are absent from spherical core/shell structures and infinitely long core/shell nanowires.

In the system we studied, a CdSe spherical core is embedded in a CdS nanorod. We first used the valence force field (VFF) method to relax the atomic positions. The charge patching method is then used to construct the ab initio DFT quality charge density of the nanosystem. This charge density is then used to calculate the local density approximation (LDA) potential in the single particle Schrödinger’s equation. To overcome the well-known band gap problem of the LDA, we have modified the nonlocal parts of the pseudopotential so that the band gaps and effective masses of the resulting bulks system are correct [5]. We call the final Hamiltonian the LDA+C Hamiltonian. The band edge states of this LDA+C Hamiltonian is solved using our folded spectrum method (FSM)[6].

We have studied two nanorods with different surface passivations. Although both passivations are not realistic, they do provide idealistic models for different type of passivations. Realistic passivation modeling is not possible at this time since the atomic detail of the real passivation is not known. In our first model passivation, both Cd atoms and S atoms exist at the

![Figure 1. ZnO/ZnS core/shell nanowire (a), and the optical absorption spectrum of the nanowire (b). The core is ZnO while the shell is ZnS. The vertical dashed lines in (b) indicate the band gap of the corresponding bulk, while the planar ZnO/ZnS indicates the band gap of a ZnO/ZnS planar superlattice.](image1)

![Figure 2. Valence band maximum (VBM) wave function (a) and conduction band minimum (b) states of the ZnO/ZnS nanowire.](image2)
surface, and any atom with only one bond connected to the rest of the nanorod is removed; we will call this model Cd+S termination model hereafter. The surface atoms are then passivated with pseudo hydrogen atoms. For Cd, it is passivated by hydrogen atoms with 1.5 electron, while for S, it is passivated by hydrogen atoms with 0.5 electron. These hydrogen atoms are placed at the centers of the cut-off bonds at the surface. In our second passivation model, only Cd atoms are at the surface, including Cd atoms with only one bond connecting to the rest of the nanorod; we will call this the Cd termination model. The main difference of these two models is that they provide very different overall dipole moment of the system. In the Cd+S model, since the surface Cd-H and S-H bonds (especially at the periphery) are very different, each of these bonds provides a small dipole moment, and they sum up to give a large net surface dipole moment. This surface dipole moment will induce an internal electric field, which will strongly affect the internal electronic structure of the system. On the other hand, the bond dipoles of the Cd termination model cancel each other out among different bond directions. As a result, its net surface dipole moment is negligibly small.

In figure 3, we show the VBM and CBM states of the Cd terminated core/rod. As we can see, the hole state is completely localized inside the CdSe core, while the electron has been pushed outside the core, far away in the CdS rod. Note that, in the natural band alignment (e.g., if both CdSe and CdS have their fully relaxed natural lattice constants), the bulk CdS CBM state is above the bulk CdSe CBM state. Thus the electron should be inside the CdSe material. In the core/rod structure, however, the CdSe is compressed from its bulk lattice constant, as a result, its bulk CBM level has been pushed up, above the bulk CdS level. As a result, the electron state is located in the CdS. It is away from the CdSe core due to the quantum confinement effect. In figure 4, we show the VBM and CBM states of the Cd+S terminated core/rod structure. The hole wave function is still inside the CdSe core, but now the electron wave function is much closer to the CdSe core. The reason is that the surface dipole moment of this system has provided an internal electric field, which pushes the electron to the right hand side, toward the CdSe core. Through this example, we see that how one can use band alignment, strain, dipole moment, and quantum confinement to manipulate the electron and hole localization, which is critical for many device applications.
3. Internal electric field and dipole moment of nanorods
As demonstrated in the example of the CdSe core inside a CdS nanorod, the dipole moment of the nanosystem can play an important role in the electronic structure of the system. We therefore carried out a detailed study of the dipole moment in nanocrystalline. To do this, we have used our newly developed linear scaling three dimensional fragment method (LS3DF) [7]. This method divides a nanosystem into small fragments with each fragment containing less than 100 atoms. The fragments are mutually overlapped, and their surfaces are artificially passivated. After the charge densities of all the fragments are calculated, they are patched together with both positive and negative prefactors. The negative fragments are used so that the effects of the artificial boundaries due to the subdivision can be cancelled out among different fragments. The global potential of the whole system is solved selfconsistently with the patched global charge density via a Poisson equation. Since the computationally expensive Schrodinger’s equations are solved only for each individual fragments, the whole calculation scales linearly to the number of fragments, thus to the size of the system. The calculation can also be massively parallelized due to the independence of the Schrodinger’s equation for different fragments. Our LS3DF code has been run on the near full Cray XT4 Franklin machine with 17,280 processors at NERSC and has reached 35 Tflops, which is 40% of its theoretical peak [8].

We used the LS3DF code to calculate the self-consistent charge density and the corresponding dipole moments of the CdSe nanorods. To study the effects of different surface passivations, we used the Cd+Se termination, and Cd only termination as described in the previous section. Again, pseudo-hydrogen atoms are used to saturate the dangling bonds. To study the effect of permanent bulk dipole contribution, we tested zinc blend (ZB) bulk crystal structure and wurtzite (WZ) crystal structure. These four systems are depicted in figure 5. They are system-1, Cd_{954}Se_{718}, ZB structure, Cd-terminated; system-2, Cd_{961}Se_{724}, WZ structure, Cd-terminated; system-3, Cd_{715}Se_{718}, ZB structure,
Cd+Se terminated, Cd$_{114}$Se$_{234}$; system-4, WZ structure, Cd+Se terminated. Their calculated total dipole moments are -13.1, 71.0, -21.5, 51.8 a.u., respectively. To show the effects of these dipole moments, we plotted the electron and hole wavefunctions of the system-2 in figure 6. As one can see, the electron and hole are localized at completely the opposite ends of the nanorod due to the internal electric field induced by the total dipole moment of the system.

4. Electron and hole states in P3HT

There are many nanostructure electronic and optical applications that involve both inorganic nanocrystalline and organic polymers. Thus, it will be interesting to calculate the electronic structures of the organic polymers in the same footing as we calculate the inorganic semiconductor nanocrystallines. Recently, we have applied our charge patching method to organic polymers [9]. The accuracy we obtained is similar to that of inorganic nanocrystals, which is 20-30 meV in the absolute eigen energy error. The error for the eigen energy differences among adjacent states is much smaller, typically in a few meV.

Poly(3-hexylthiophene) P3HT is an often-used organic polymer for electronic and optical applications. After annealing, P3HT likes to form local plate like crystal domains, and between the domains they are also amorphous like structure. While the electronic structure of the perfect crystal can be studied easily by small system direct ab initio calculations, the electronic structures in the amorphouslike regions are more difficult to be calculated. Here we have applied our CPM to study the electronic structures in such amorphous regions. The empirical force field method, which is accurate in describing the nonchemical interactions between the polymers, is used in molecular dynamics simulation and simulated annealing to obtain the morphologies and atomic structures of the polymers. Once the atomic positions are obtained, CPM is applied to get the charge density of the system. As in the inorganic nanocrystalline, the charge density is then used to calculate the potential of the system, and the folded spectrum method [6] is used to calculate the band edge states.

Figure 7 shows the atomic structures of the P3HT molecules and the corresponding conduction band states. In the calculation, there are 5 P3HT chains, each with 20 pentagon units. In total, there are 2510 atoms. They are placed in a periodic supercell with the average density equal
to that of the usual P3HT polymer blend. Simulated annealing is performed based on the empirical force field, and the amorphous state atomic structures are obtained. In figures 7 and 8, for clarity, only the main P3HT chains are shown, not the side chains. The seven conduction band states shown in figure 7 have an average energy separation of about 30 meV. Figure 8 shows the first seven valence band states for the same molecule configuration as in figure 7. The average energy separations between these seven valence states is about 43 meV, which is larger than the corresponding conduction band value. In figures 7 and 8, the isosurface for each state encloses 50% of its electron charge. From figures 7 and 8, we can see that the wave functions are localized to 2 or 3 pentagon units in most cases. They are not extended to all the units in a given chain. Besides, there are strong correlations between electron and hole states. That means if a segment is good for a band edge electron state, it is probably also good for a band edge hole state. The localizations of the electron and hole states will have significant impacts on their mobilities. Our calculations shed light on the electronic properties of this widely used, yet poorly understood complicated polymer system.

5. Conclusion
Energy applications of nanostructures require the understanding of their electronic structures and optical properties. We have developed a comprehensive approach to study such properties, especially for electrons, hole localizations, quantum confinement effects, and optical properties. In the current paper, we have demonstrated how to use our approach to study these properties for different systems with ab initio accuracy. Our approach includes a non-self-consistent charge patching method and self-consistent linear scaling three-dimensional fragment method. With massively parallel computers, it is now possible to calculate thousand-atom nanosystems on a routine basis. This is a major achievement compared to ten years ago, when thousand-atom systems could be calculated only with empirical pseudopotentials or with tight-binding models.

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