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Classical versus *ab initio* structural relaxation: electronic excitations and optical properties of Ge nanocrystals embedded in an SiC matrix

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Abstract

We discuss and test a combined method to efficiently perform ground-state and excited-state calculations for relaxed structures using both a quantum first-principles approach and a classical molecular-dynamics scheme. We apply this method to calculate the ground state, the optical properties, and the electronic excitations of Ge nanoparticles embedded in a cubic SiC matrix. Classical molecular dynamics is used to relax the large-supercell system. First-principles quantum techniques are then used to calculate the electronic structure and, in turn, the electronic excitation and optical properties. The proposed procedure is tested with data resulting from a full first-principles scheme. The agreement is quantitatively discussed between the results after the two computational paths with respect to the structure, the optical properties, and the electronic excitations. The combined method is shown to be applicable to embedded nanocrystals in large simulation cells for which the first-principles treatment of the ionic relaxation is presently out of reach, whereas the electronic, optical and excitation properties can already be obtained *ab initio*. The errors incurred from the relaxed structure are found to be non-negligible but controllable.

1. Introduction

The physics of nanoparticles presents particularly interesting aspects, mainly with respect to the strong modifications of the fundamental properties of the material due to the spatial confinement in three dimensions. Noticeable effects on the joint density of states and on the optical absorption and luminescence spectra have been predicted and observed (see, for example, [1, 2]). Even optical gain has been demonstrated in Si nanocrystals [3].

Over the last few years it became possible to perform first-principles (*ab initio*) quantum simulations for large systems including the calculation of their optical and electronic excitation properties [4, 5]. Several publications report quantum calculations of ground-state properties of large simulation cells of up to 512, or, singularly, up to 2744 atoms [5–9]. However, in the *ab initio* calculations of large systems, the structural relaxation is, more often than not, the most time-consuming part, determining the feasibility of a given simulation. In order to calculate the properties of rather large systems of technological importance, being of the order of, for example, 2–5 nm, it is necessary to overcome these limitations. One possibility, which to date has customarily been used, is the determination of excitation properties maintaining the unrelaxed atomic positions [4, 6, 10]. However, the optical absorption and electron excitation energies depend sensitively upon the relaxed structure of the crystal [11, 12]. For example, the value of the bulk band gap in semiconductors can be dramatically affected by the lattice parameters used in the calculation [13]. It has also been demonstrated that the inclusion of the structural relaxation is indispensable for a correct description of the nanocrystal properties [14].

Several authors have used combined methods of classical and quantum calculations in order to determine the ground-state properties of nanometre-size structures (see, for example, [15]), without, however, investigating in detail the errors arising from the combination of the methods. There is agreement in the field that the classical methods are better than nothing but not as good as *ab initio* calculations, but it remains to be demonstrated that this means ‘good enough’ for nanometre-sized embedded systems. The present paper aims to provide this demonstration. We apply one possible combined procedure and test it quantitatively for a model system for both ground-state and excited-state properties. To our knowledge, this is the first detailed comparison between relaxation schemes with respect to the optical and excitation properties of embedded nanocrystals. The combined method makes it possible to include the ionic relaxation in the calculation of the optical and electronic properties for large systems for which it is still not possible to do ionic relaxation by full quantum first-principles methods, whereas *ab initio* calculations for a fixed geometry are already feasible. Examples are large cluster systems, surfaces, and nanotubes.

2. Methods

The combined procedure can be outlined as follows. Given a certain large system (cluster, nanocrystal) one starts from the ideal atomic positions which correspond to the bulk geometry and performs a model-potential molecular-dynamics (MPMD) simulation to determine the relaxed configuration. Afterwards, these coordinates are taken as the input in the determination of the ground-state properties (e.g., total energy, eigenvalues and eigenfunctions, valence charge density, etc) at the DFT-LDA level. Once the ground-state properties have been determined one can calculate the optical properties, for example within DFT-LDA [16], or the electronic excitation spectrum, for example within the GW scheme [4, 17, 18]. In figure 1 we outline the flowchart of the combined method. We also indicate the path relative to the full *ab initio* procedure which is rather time-consuming for huge simulation cells (path B in figure 1). This path is, however, only used in the present manuscript to provide a reference for the test of the MPMD method. This procedure is very advantageous because the difference is now restricted to the relaxation while the electronic-structure calculation is done using exactly the same methods.

For the sake of comparison we chose a model system of an intermediate cell size for which it has been possible to follow all the steps within a quantum first-principles (FP) approach. On the other hand the system already exhibits the typical properties of an embedded nanocrystallite. Our model system consists of a 216-atom SiC supercell in which 17 host material atoms

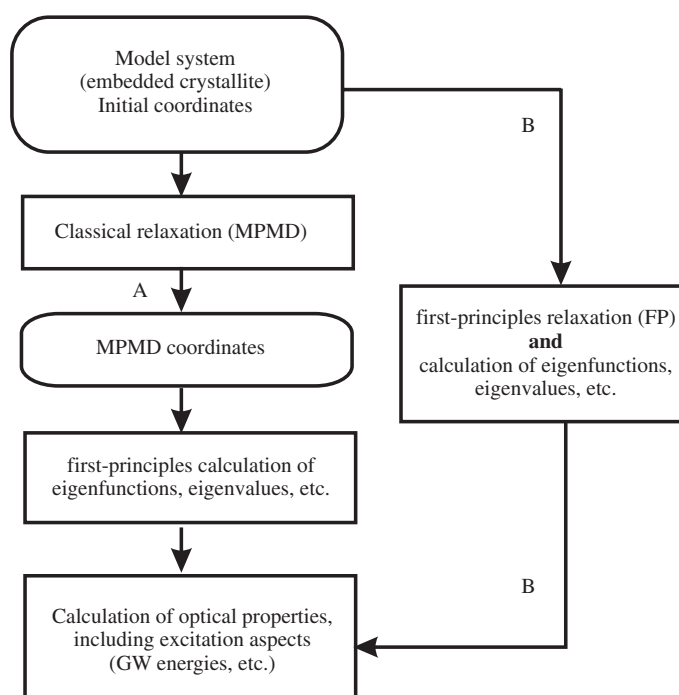


Figure 1. Flowchart outlining both the combined procedure (path A) and the full first-principles procedure (path B) which has been used to make the quantitative comparison of the present paper.

(Si and C) are replaced by one Ge atom each. Starting from one Si atom and replacing nearest neighbours shell by shell one obtains an ideal structure of a highly strained quasi-spherical [14] Ge nanocrystal embedded in an SiC matrix, having Ge–C interface bonds. The point group of the supercell system is still T_d . The optical properties of the unrelaxed [6] and of the relaxed [19] system have been reported before, as well as its GW band structure [4].

Moreover, the system is a good test for the method because it is strongly strained due to the large lattice mismatch. We have performed a parallel analysis of the calculated properties and, hence, of feasibility and efficiency of the combined scheme. Comparison of optical and electronic excitation energies calculated by means of both the full *ab initio* and the combined method has been performed.

A strong reduction of computational time results within the combined method. The computer time needed to perform the ionic relaxation within an *ab initio* method depends strongly on the cell size. While for a relatively small system like that treated here it takes, using the VASP package, between 10 and 20 h on a RISC workstation to relax (216 atoms, making use of the symmetry and using only one \mathbf{k} point (not Γ) [19]), the relaxation of a similar system in a 512-atom cell takes roughly 100 h on two processors. The largest cell relaxed to date, containing 2744 atoms [8], required two months on 32 processors on an HP parallel machine. For the MPMD calculations, the relaxation times are rather of the order of a few hours or less. Thus by using the combined method at least a two-orders-of-magnitude reduction results. Due to the different scaling of FP and MPMD calculations, the reduction is the stronger the larger the cell sizes are.

For the MPMD relaxation procedure we adopted the Tersoff potential [20–22]. The calculations have been performed at constant volume, and we typically annealed the system

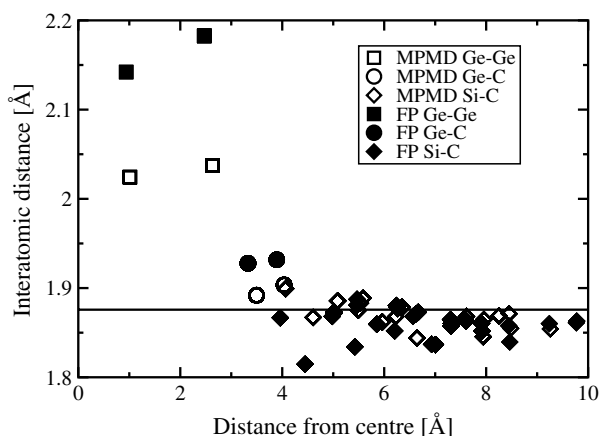


Figure 2. Interatomic distances (i.e., bond lengths) after the relaxation as a function of the distance of the centre of the bond from the centre of the crystallite. The empty symbols represent the MPMD results while the filled symbols indicate those of the FP calculations. The horizontal line represents the interatomic distance in the unperturbed SiC crystal with its theoretical lattice constant of 4.334 Å.

up to 800 K during a thermal cycle as long as 12 000–15 000 time steps. The time step was as short as 0.5 fs for an optimal integration of the equations of motion. Atomic trajectories have been computed by means of the velocity-Verlet algorithm. In the non-relaxed configuration the formation energy is -5.81 eV/atom, while after relaxation we obtain -5.92 eV/atom. Furthermore we obtain -6.18 eV/atom for pure SiC and -3.85 eV/atom for Ge (at its equilibrium lattice constant 5.66 Å). Thus the average formation energy of 17 Ge atoms plus 199 (95 Si and 104 C) atoms of SiC in a separate phase is -6.00 eV/atom, and the formation energy of the cluster is 0.08 eV/atom.

For the *ab initio* calculations we use the VASP package [23, 24] in the way presented in [6, 19]. The electronic-structure calculations are done within density-functional theory in the local-density approximation (DFT-LDA) using the projector-augmented wave method (PAW) [25] in order to treat very large cells. The ionic relaxation is done by means of a quasi-Newton method until all the forces are smaller than 0.003 eV Å $^{-1}$. The optical calculations are performed within the independent-particle picture [26, 27]. Matrix elements follow from all-electron wavefunctions obtained by means of the PAW method [25, 28]. For the Brillouin zone integration an extrapolative variant of the tetrahedron method is applied [4, 5]. No extra broadening is applied. The inclusion of self-energy effects in the calculation of the band structures and optical spectra is done using the GW method as presented in detail in [4].

3. Structure

In figure 2 we show the bond lengths of the system as a function of the distance of the centre of the bond from the centre of the crystallite. Due to the symmetry, every point represents a number of bonds which have both the same lengths and the same distance from the centre. No attempt has been made to show this multiplicity in the figure. Obviously, the deviation from the SiC bond lengths is strongest for the strained Ge–Ge bonds within the Ge cluster, the bonds of which are compressed very strongly with respect to their equilibrium lengths. The Ge–C interface bonds approach already the lengths of the SiC bonds. The matrix further away from the cluster is compressed due to the expansion of the cluster at the centre of the

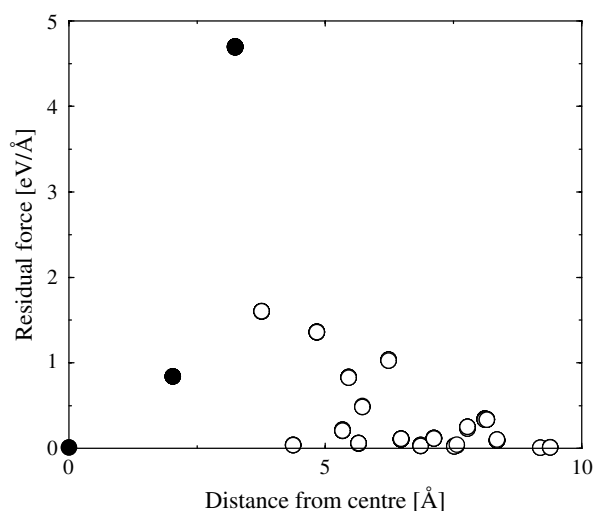


Figure 3. Residual forces after the classical relaxation as a function of the distance of the respective atom from the centre of the crystallite. The empty symbols represent the matrix atoms while the filled symbols indicate Ge.

cell. Our results indicate that the MPMD results reproduce qualitatively the results of our FP calculations. While the agreement is not perfect, the direction of the changes with respect to the unrelaxed structure is given correctly.

In order to obtain a precise picture of the situation, we show the residual forces of the MPMD treatment in figure 3. To do that, we use the atomic positions resulting from the classical calculation, and calculate the forces using the *ab initio* method without ionic relaxation. Only these forces are shown. The reference value pertaining to the *ab initio* method are naturally all below the force tolerance of the calculations. On the scale of figure 3 they are indistinguishable from zero.

While the zero force on the centre Ge atom of the crystallite is due to the symmetry of the system, relatively strong forces remain in the two shells of Ge atoms around the centre atom as well as in the adjacent matrix atoms. These forces can serve as an estimate of how well the MPMD method relaxes the structure when one considers the *ab initio* results as an error-free reference. The largest errors occur in the interface region. A decrease is found towards the boundary of the supercell where the situation is very close to the unstrained bulk of the matrix material. The largest errors thus occur in the most strongly strained parts of the system. As realistic systems are expected to be somewhat larger and to involve less strain [29], the method should for those fare better than for the present, highly strained model system. On the other hand, shortcomings of the description of the (Ge–C) interface bonds may have contributed substantially to the errors.

Comparison of the forces in figure 3 with the interatomic distances in figure 2 shows the correspondence of the two quantities. The forces are largest on those atoms where the deviation of the MPMD positions from the *ab initio* positions is largest.

The residual forces thus yield important information on the quality of the MPMD relaxation. However, they have only an indirect bearing on the electronic and optical quantities one is interested in in the modelling of the nanostructures. We have to compare the latter quantities in order to demonstrate the feasibility of the combined method.

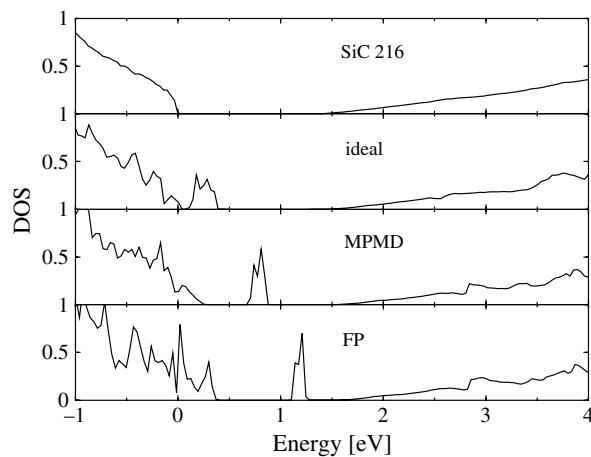


Figure 4. Density of states for the pure matrix SiC, the unrelaxed cluster of 17 Ge atoms embedded in SiC in the 216-atom supercell, and the results for the MPMD and the FP relaxation. The gap states are occupied.

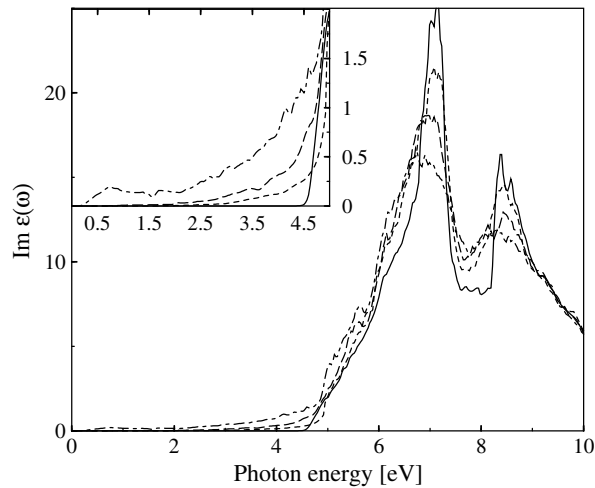


Figure 5. Imaginary part of the dielectric function for the pure host material (solid curve), the unrelaxed supercell system (dashed), and for the MPMD-relaxed (long-dashed) and the FP result (dot-dashed). The inset shows an enlargement of the region below the onset of the absorption of the matrix.

4. Electronic properties

In figure 4 we show the density of states obtained for the different geometries, the unrelaxed structure, and the MPMD and the FP results. The DOS of the pure SiC is modified by the inclusion of the nanocrystal. In particular, a peak within the band gap near the top of the valence band appears. This is due to states localized in the Ge domain [6]. The result of the ionic relaxation is an upwards shift of the gap states with respect to the matrix band edges. Again, the MPMD relaxation leads to results which point in the correct direction, if the unrelaxed structure is taken as a reference.

In figure 5 we report the imaginary part of the macroscopic dielectric function calculated within DFT-LDA [5, 6, 16]. The inclusion of the Ge cluster into the SiC matrix results in a

lowering of the main peaks and a slight near-rigid red-shift of the first slope. Moreover, below the onset of the pure-SiC absorption, there arise contributions due to transitions involving the gap states [6]. The relaxation enhances these effects.

Again, and in accordance with the findings about the bond lengths in figure 2, the change as found for the MPMD structure points in the right direction but does not quite attain the values of the FP results. Furthermore, the relatively strong difference between the MPMD and the FP results, clearly shown in the inset in figure 5, can be understood in view of the strain-like representation in figure 2. This part of the spectrum is determined mostly by the contributions of the gap states which, in turn, are due to states localized in the Ge region [6]. As can be seen from figure 2, in this region the difference between the bond lengths given by the two relaxation methods is quite large, representing a significant difference in local pressure (or strain) which is underestimated by the MPMD method, as compared to the FP relaxation. Thus the strong pressure dependence of the Ge crystallite spectra [30] is here giving rise to the differences between the results of the two methods. It can be directly concluded that for less strained systems the MPMD method should work better.

5. Excitation energies

The calculation of the optical properties of nanostructures needs to go beyond the ground-state single-particle description by means of DFT. This is due to the fact that the optical properties are due to excitations of the system. For that reason, a complete description will have to include the self-energy effects describing the reaction of the remaining electrons to the excitation.

Excitation now has different effects. In strongly localized systems, the Frank–Condon-like (ionic) relaxation mechanism creates a contribution to the luminescence Stokes shift [31–33]. However, for the less strongly localized electronic states this effect is very small. We do not consider it here.

While for strongly confined systems the self-energy effects have been found to cancel substantially with Coulomb effects [34], for bulk systems and less strongly confined structures they are important. The Kohn–Sham energies can be shown to present a well-defined approximation to the excitation energies [35]. Here we calculate excitation energies in the GW approximation. This is important for the evaluation of the MPMD method because GW band structures can be highly sensitive to changes in the structural configuration [11, 13].

In figures 6 and 7 we show the LDA and GW band structures of the unrelaxed and the relaxed systems. As mentioned before, the crystallite introduces occupied gap states into the band structure of the host [6]. The physical effect of the relaxation is an upward shift of these gap states, much in accordance with the findings with respect to the DOS. The change of the host gap, as far as is discernible from the band structures, is less strong. Again it is apparent that the results according to the MPMD lie between the unrelaxed and the FP results. The latter fact is also true for the GW band structures. This has not been *a priori* clear because of the known sensitivity of the GW band structures to changes in the structural configuration [11, 13]. However, our results indicate the feasibility of the combined method also for the calculation of GW bands and, hence, one-particle spectra.

6. Conclusions

In conclusion, we have quantitatively tested a combined method to efficiently perform ground-state and excited-state calculations for large simulation cells using a classical molecular-dynamics approach for the ionic relaxation and an *ab initio* scheme for the electronic-structure,

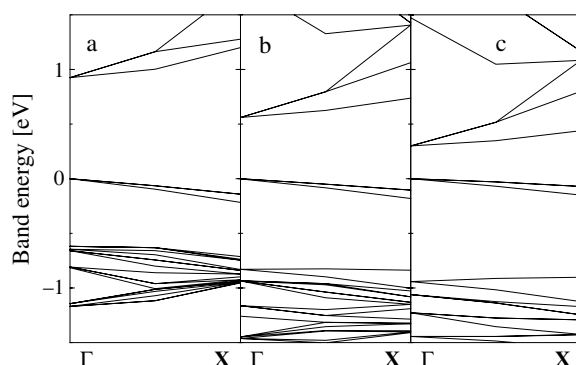


Figure 6. LDA band structure along the Γ -X direction for the unrelaxed (a), the MPMD-relaxed (b) and the FP-relaxed (c) structures. The energy of the gap states at Γ has been chosen as the energy zero in order to make the differences in the relative position of the Ge-determined gap states easily perceptible.

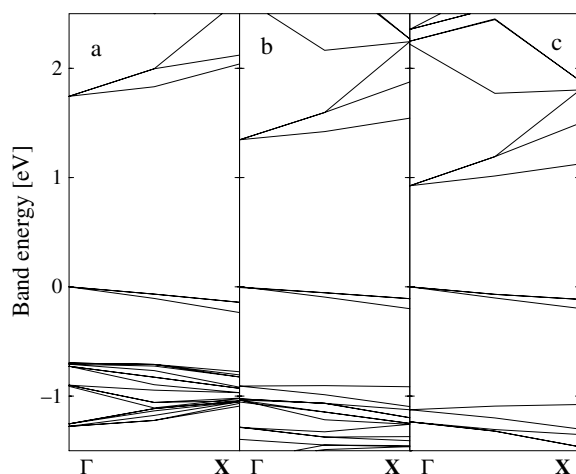


Figure 7. GW band structure for the unrelaxed (a), the MPMD-relaxed (b) and the FP-relaxed (c) structures. The energy zero has been chosen as in figure 6.

optical, and excited-state calculations. Depending on the cell size, a reduction of computer time by about two orders of magnitude or even more can be achieved.

We tested a small, strongly strained Ge crystallite embedded in SiC as a model system which had been investigated previously. Since the main deviations of the MPMD results can be traced back to the strongly strained region of the Ge crystallite, it is definitely expected that the method fares better for larger, less strained systems.

All the results are qualitatively correct, although non-negligible errors due to the imperfect relaxation arise. Naturally, the quality of the model potential is crucial to achieve qualitative agreement with FP calculations, especially with respect to the states localized in the interface region. The general conclusion drawn from the tests is that the combined method provides a feasible tool for the description of a wide range of properties, including the electronic DOS and band structure and even the excitation aspects as described by the self-energy corrections within the GW approximation. This means in particular that large supercells can be treated

where the *ab initio* ionic relaxation is practically out of reach while the excitations and optical properties can already be calculated for one fixed geometry by means of *ab initio* procedures.

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