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Global Minimum Determination of the Born-Oppenheimer Surface within Density Functional Theory

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We present a novel method, which we refer to as the dual minima hopping method, that allows us to find the global minimum of the potential energy surface (PES) within density functional theory for systems where a fast but less accurate calculation of the PES is possible. This method can rapidly find the ground state configuration of clusters and other complex systems with present day computer power by performing a systematic search. We apply the new method to silicon clusters. Even though these systems have already been extensively studied by other methods, we find new global minimum candidates for Si_{16} and Si_{19}, as well as new low-lying isomers for Si_{16}, Si_{17}, and Si_{18}.

Determining the structure of a molecule, cluster, or crystal is one of the most fundamental and important tasks in solid state physics and chemistry. Practically all physical properties of a system depend on its structure. The structural configurations of a system are determined by the Born-Oppenheimer potential energy surface (PES), which gives the energy of a system as a function of its atomic coordinates. Minima of the PES give stable configurations. The global minimum gives the ground state configuration. At low enough temperature the system will be found in this global minimum structure assuming that this structure is kinetically accessible. Since the zero-point energy of different structures varies negligibly, the determination of the ground state structure is equivalent to the mathematical problem of finding the global minimum of the PES.

It is well established that the PES of a condensed matter system can be calculated with good accuracy within density functional theory (DFT). Nevertheless, DFT methods have not been used up to now as a standard tool in algorithms that attempt to determine the ground state of complex systems because most algorithms for the determination of the global minimum require an enormous number of evaluations of the PES. Since each evaluation requires a full electronic structure calculation, these algorithms are computationally too demanding within the full DFT framework. A systematic search for the global minimum is, however, possible with cheaper methods such as tight binding and force field methods.

In summary, with present methods one has the choice either of using methods with a limited power of predictability or of doing a constrained search for the global minimum. In a constrained search one fixes some atomic positions or imposes some structural motifs, but experience shows that the global minimum is often missed in this way. To overcome this dilemma, several researchers have

adopted an approach where one first effectuates a systematic search with a method that allows for a fast but inaccurate calculation of the PES to obtain some candidate structures. Which of the candidate structures is lowest in energy is determined in a second step by DFT calculations. As we show later, this approach is generally not applicable.

Other researchers have combined systematic search algorithms with DFT methods, but their algorithms required too many DFT calculations to be computationally feasible if one wants to find the global minimum. Röthlisberger *et al.* [1] have used simulated annealing within DFT to find structural motifs of the midsize clusters, but their final lowest energy geometries were obtained by other means. Yoo and Zeng [2,3] have combined basin-hopping (BH) with DFT and were able to find new low-lying minima for some clusters, among them Si_{16}, Si_{17}, and Si_{18}. For Si_{16}, they have found a new global minimum structure by performing a systematic BH search within DFT. Both the systematic BH for Si_{16} as well as the constrained BH for Si_{17} and Si_{18} within DFT have missed the global minimum.

In this Letter we present a method that allows for a systematic search for the global minimum of the PES of a complex system within DFT. The method is a modification of the minima hopping method (MHM) [4]. In the MHM one visits a series of local minima until the global minimum is found. The algorithm has a double loop structure. In the inner loop one attempts to escape from the current minimum, and in the outer loop one accepts or rejects new minima found by successful escape attempts. A *history list* keeps track of all minima found. A feedback mechanism uses information from this history list to make more vigorous escape attempts when the algorithm is revisiting previously found minima, thereby preventing the algorithm from getting trapped in an incorrect minimum. The inner escape loop contains two basic steps. The

first does a certain number of molecular dynamics (MD) moves until one has overcome at least one energy barrier. The second step consists in performing a standard geometry relaxation to reach the closest minimum with an accurate method.

In the ordinary version of the MHM [4] the forces for the MD and for the geometry optimization part are done with the same method. Fast methods such as force field or tight binding methods have to be used to limit the computing time to an acceptable length. In the modified MHM presented in this Letter two different methods are combined: a slow but accurate method and a fast but less accurate method. The fast method is used for the MD part and for the first few steps of the geometry optimization. The accurate method is then used for the final geometry optimization and the evaluation of the energy of the relaxed structure. In this way the search for the global minimum is reduced to a relatively small number of geometry optimizations with the accurate and expensive method plus a much larger number of force evaluations with the fast method. Henceforth, we refer to this modified minima hopping algorithm, which combines the two methods for the calculation of the forces, as the dual minima hopping method.

The fact that the input configuration for the geometry optimization with the accurate method is a configuration that was prerelaxed with the fast method is important for the stability of the entire algorithm if the accurate method is a DFT method. DFT programs typically do not converge if the input configuration is far from any physically reasonable configuration. The prerelaxation with the fast method excludes the possibility that a physically unreasonable state is used as an input configuration. From the previous considerations it might seem advantageous to do a full prerelaxation, i.e., to use a minimum of the fast method as the input for the geometry optimization with the accurate method. If the fast method is a reasonable approximation, then a local minimum found by it will often be close to a local minimum of the accurate method.

Unfortunately, in general there is no one-to-one correspondence between minima obtained from the two methods. Therefore, some minima obtained using the accurate method are inaccessible from the starting configurations provided by the fast method. For this reason only a small number of steps should be done in the prerelaxation with the fast method. In this way the ensemble of the starting configurations for the geometry optimization with the accurate method comprises a considerable part of the configurational space (and not only the ensemble of all the minima of the fast method), and one can reach virtually any minimum of the accurate method.

The Bell-Evans-Polanyi (BEP) principle [5] states that highly exothermic chemical reactions have a low activation energy. In the context of a global minimum search, this means energetically low configurations will preferably be found behind low energy barriers. The BEP principle is essential for the success of the MHM as has been shown in [4]. The correlation between the barrier height and the energy of the minimum "behind" the barrier certainly deteriorates if one is combining two different methods. This implies more local minima will be visited, on average, with the dual minima hopping method (DMHM) before the global minimum is found than with the ordinary MHM. In order to explore the influence of this reduced correlation we did systematic tests with a 38 atom Lennard-Jones (LJ) cluster. This is a system for which the global minimum is hard to find since it is contained in a small secondary funnel [6], but the computing time is small since the potential can be evaluated very rapidly. As the accurate method we used the LJ potential. As the "fast" method we used a truncated polynomial approximation of the LJ potential as shown in Fig. 1. As expected, the number of local minima that are visited on average before the global minimum is found increases from 380 to 530; nevertheless, the number of force evaluations needed with the "expensive" exact LJ method is reduced by a factor of 5.

To demonstrate that the DMHM can, indeed, find the global ground state geometry of real clusters, we have applied it to silicon clusters. Numerous groups are involved in the search of the ground state of silicon clusters, and there are at least 50 theoretical papers on this subject [1–3,7–17]. Applying DMHM to silicon clusters, we were able to find within several days of computing time all of the known structures [9–12] in the range Si_4-Si_{19}, and we even found lower energy structures for Si_{16} and Si_{19} in spite of the fact that silicon clusters up to 19 atoms in size have already been extensively studied. The new global minimum structures within CPMD-PBE (see below) Si_{16a} and Si_{19a} as well as the new low-lying isomers Si_{16b}, Si_{17a}, Si_{17b}, and Si_{18a} are shown in Fig. 2. The structure Si_{16a} contains the tricapped trigonal prism (TTP)-Si_9 subunit [18] and is compact in contrast to the structure Si_{16} reported by Zeng [3]. The structure Si_{19a} consists of a TTP-Si_9 subunit and a Si_{10} subunit. The low-lying isomer
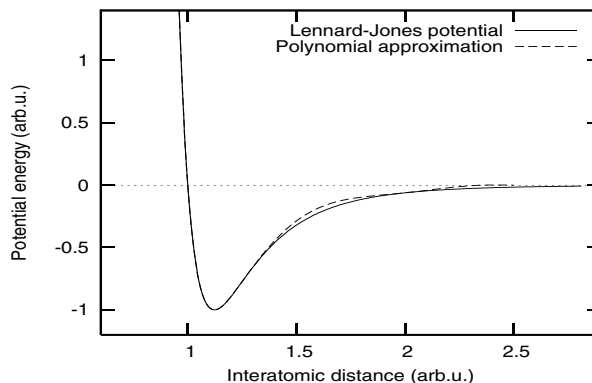

FIG. 1. The truncated polynomial approximation of the Lennard-Jones potential and the exact Lennard-Jones potential.
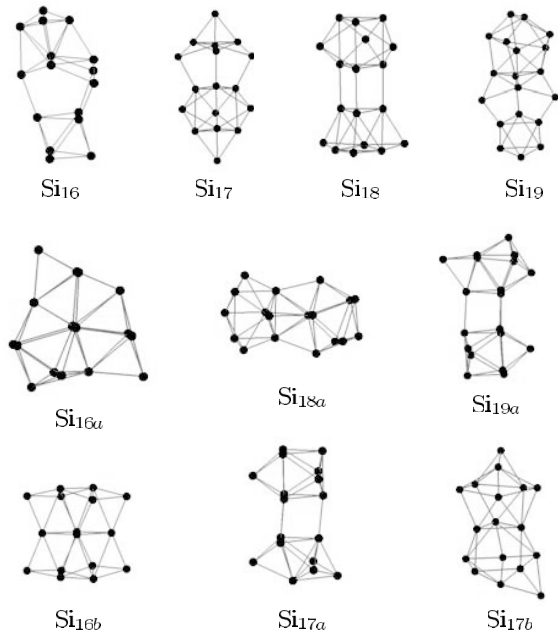
FIG. 2. New low energy geometries Si_{16a}, Si_{16b}, Si_{17a}, Si_{17b}, Si_{18a}, and Si_{19a} found in this work with DMHM and the putative global minimum structures Si_{16} [3], Si_{17} [7], Si_{18} [7], and Si_{19} [13] reported previously and reproduced by the DMHM. The new geometries will be posted on the Cambridge Cluster Database [24].

Si_{16b} is compact and highly symmetric. The low-lying isomer Si_{17a} consists of a TTP-Si_9 subunit and a Si_8 subunit. The low-lying isomer Si_{17b} consists of two equal 7-blocks, which are rotated against each other, and a triangle as a cleaving block. The structure Si_{18a} is prolate and consists of two TTP-Si_9 subunits that are rotated against each other. In contrast to the previous works, the new configurations as well as the putative global minimum structures reported previously were found by the DMHM automatically after having visited only a few hundred local minima.

As the fast method, we have used the Lenosky tight binding scheme for silicon [19]. The accurate method is DFT as implemented in the QUICKSTEP code [20]. After having performed the DMHM with QUICKSTEP using a relatively small Gaussian basis set and the local density approximation, we have calculated accurate final energies and zero-point energies with the CPMD program [21] using the PBE functional [22], a high accuracy pseudopotential [23], large supercells (24 Å), and a sufficient plane wave cutoff (28 Ry). The results for the various clusters as compared to Si_{16}, Si_{17}, Si_{18}, and Si_{19} are presented in Table I. In contrast to other exchange-correlation functionals, the PBE functional [22] was not fitted to any chemical systems with simple bond structures and is expected to give the most accurate description of the complex bonding patterns found in silicon clusters. The term "ac-

TABLE I. The energy differences in eV without and with zero-point energy correction between the new low energy geometries Si_{16a}, Si_{16b}, Si_{17a}, Si_{17b}, Si_{18a}, and Si_{19a} found in this work with DMHM and the putative global minimum structures Si_{16} [3], Si_{17} [7], Si_{18} [7], and Si_{19} [13] reported previously using the PBE exchange-correlation functional as implemented in CPMD.

Cluster	Si_{16a}	Si_{16b}	Si_{17a}	Si_{17b}	Si_{18a}	Si_{19a}
PBE	−0.15	0.02	0.08	0.20	0.24	−0.08
PBE(Z)	−0.16	0.01	0.09	0.23	0.19	−0.09

curate" must be handled with caution, however, since DFT is only an approximation and, as a matter of fact, the energetic ordering may change if one uses different functionals [12].

Among the various force fields and tight binding schemes we have tested, the Lenosky tight binding scheme [19] gave the best agreement with the DFT energies. It can predict the DFT energies with an error of roughly 1 eV as shown in Fig. 3. Figure 3 also shows why the common approach of first finding candidate structures by doing a systematic search with a cheap method and then checking by an accurate method which of the candidate structures gives the global minimum is problematic except for very small systems. For a 25 atom silicon cluster the number of geometric configurations within 1 eV above the ground state is of the order of 10^4 states, for a 33 atom cluster it is already of the order of 10^5 states, and it increases exponentially with system size. It is therefore virtually impossible to check which one of these 10^4 to 10^5 con-
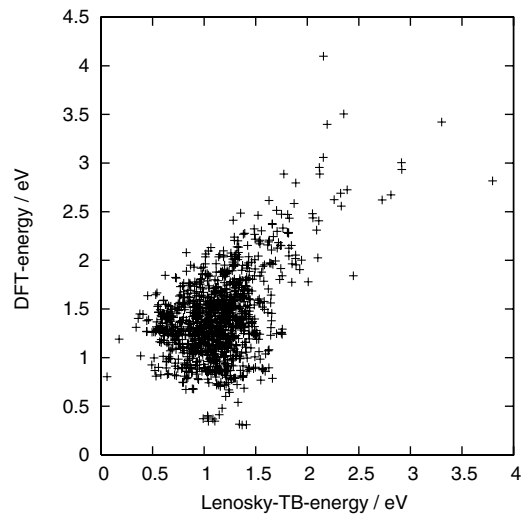

FIG. 3. The correlation between tight binding and density functional energies for various configurations of a Si_{25} cluster. If the correlation was perfect, all the points would lie on the diagonal. Instead, the scattering shows that the tight binding energies can predict the energy differences between various cluster configurations only with an error of about 1 eV.

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figurations is the global minimum in DFT. Besides, because of the absence of the one-to-one correspondence between the local minima of the fast method and of the accurate method, it is not guaranteed that any of the minima of the fast method will lead to the global minimum of the accurate method upon relaxation.

The identification of the previously visited minima is an essential ingredient of the MHM. In the context of the ordinary MHM the energy can be used to identify configurations since it is possible to calculate the energy with many significant digits both for force fields and for tight binding schemes. With DFT programs this is not any more possible because of the presence of numerical noise. For this reason, we have used in addition to the energy all interatomic distances. Two DFT minima are considered to be identical if all their interatomic distances ordered by magnitude agree to within a certain tolerance.

In summary, we have presented a method that allows one to find the global minimum of the DFT potential energy surface within acceptable computer time for moderately complex systems. The method is efficient for the following reasons. First, it requires only DFT calculations for configurations where DFT programs typically converge without problems. It does not, for instance, require DFT calculations for configurations generated by random displacements from a previous configuration. Second, the MHM is highly efficient in the sense that the number of minima visited before the ground state is found is small. Even though the DMHM is not quite as good from this perspective, it is still efficient if the fast method used for the MD part is qualitatively correct. Third, most of the force evaluations are done with the fast method and the total effort for finding the global minimum is equal to the effort of doing only an affordable number of geometry optimizations with the accurate method.

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