PHYSICAL REVIEW B **98**, 144109 (2018)

Force field preconditioned *ab initio* structure relaxation method

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(Received 11 February 2018; revised manuscript received 15 August 2018; published 16 October 2018)

We present a general method to accelerate *ab initio* atomic structural relaxations. In this method, the conjugate gradient *ab initio* relaxation is preconditioned by a force field relaxation. This force field is constructed on-the-flight with the information of the *ab initio* forces and the current atomic configuration. At each *ab initio* relaxation step, the so-constructed force field is used to prerelax the system, with the relaxation direction as the preconditioned direction for the *ab initio* conjugated gradient method. The force field model and its parameters are rather general making this method applicable for a wide range of systems commonly used in material simulations. More than 80 different systems have been tested representing different cases in material simulations. Across the board, we find accelerations mostly over a factor of 2 and for some large systems with a factor of 6 ∼ 9. There is no case where the relaxation becomes worse. The code and lib for this method are provided, which can be used as a plugin in a standard *ab initio* atomic relaxation code.

DOI: 10.1103/PhysRevB.98.144109

Ab initio calculations based on quantum chemistry methods or density functional theory (DFT) have played a more and more important role in material simulations. However, *ab initio* simulations for large systems can be rather expensive and can take an agonizingly long time to finish. The important role of *ab initio* simulation in high-performance computing can be illustrated from surveys of major computer center time usage, where it is found that the *ab initio* simulations can take about 20% of all computer time [1]. Among all *ab initio* simulations, atomic relaxation is one of the most widely used methods and can also be one of the most expensive calculations. For large systems, hundreds of steps could be needed for the calculation to converge beyond a typical minimum atomic force criterion of 0.01 eV/A. As *ab initio* methods are increasingly used for new types of simulations, e.g., the genetic algorithm search of global structure minimum [2–4], high throughput search for optimal material properties, the local minimum atomic relaxation often becomes the bottleneck for all these simulations. It will thus be tremendously helpful if the *ab initio* atomic relaxation can be sped up in some degree. Even a factor of two or three speedup could have a major impact. In this work, we present a general method to speed up the *ab initio* atomic relaxation with guidance from a simple, unified, and general classical force field. The speed up varies from 2–9, and it works for a wide range of systems from small molecules to large nanosystems.

Conjugate gradient (CG) [5] and Broyden-Fletcher-Goldfarb-Shanno (BFGS) [6] are the two most widely used methods to relax the atomic structure following the DFT energy. The speeds of these two methods are similar. While BFGS can be slightly faster in some cases, if the initial atomic position of the system is far away from the minimum, the CG method could be more stable. There are other methods, such as the steepest descent and the damped molecular dynamics method. They could be more stable, but in general are much slower. Recently, there is also a new method called FIRE [7], which combines the damped molecular dynamics with BFGS method. Such method can be useful for large difficult problems where several thousand steps are needed [7], however, for problems as the ones tested in the current paper, we found that it sensitively depends on the adjustment of the parameters [8]. With unadjusted default parameters, it could be even slower than plain CG and BFGS. This makes it difficult to use especially for automatic and high throughput calculations. In the current work, we will base our approach on the CG method, which is general, stable, and relatively fast. Note that this is a relaxation method reaching the local minimum of the energy surface, not a global minimum search method.

Our approach is based on the idea that a simple Hamiltonian might be able to guide the *ab initio* atomic relaxation. It is well known that a good preconditioning can significantly speed up the CG. For example, for a nanosystem, a preconditioner can be constructed from the bulk dynamic matrix, which significantly accelerates the atomic relaxation [9]. However, such an approach can only be applied to nanostructures with bulklike internal degree of freedoms. In previous works, it has also been found that, a proper classical force field Hamiltonian can be used to provide either the preconditioning [10,11] or curved line minimization path [8] for the CG method with a speed-up factor of 2–6. Unfortunately, most of these works require specific force fields and repeated on-the-flight fitting of the force field parameters [8,11]. In particular, while it works well for metallic systems with either embedded atom force field [12] or Lennard-Jones force field [13], it is difficult to be generalized to covalently bonded systems. Notice that, the commonly used CG or BFGS are agnostic

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regarding the physical meaning of the minimized variables (the atomic coordinates), such information (e.g., the distance between atoms) could be useful to construct approximated Hessian matrix of the system. In the current work, we present a method, which uses simple and general classical force field to provide a preconditioner for the *ab initio* atomic relaxation. More specifically, the ideal bond lengths and angle values for each individual bond and angle are calculated on-the-flight using the current atom position at each *ab initio* CG step. As a result, there is no need for their parameters, and the valence field model will have zero force. Only two generic bond strength and angle strength parameters are used. We have also combined the valence force field with embedded atom force field within a given system to deal with more complicated cases. The DFT force is used at an external force on top of the force field. This on-the-flight constructed force field potential is then used to relax the atomic position, with the resulting relaxation direction serving as the preconditioned direction of the DFT CG step. This avoids the need to calculate and invert the Hessian matrix of the force field model at every DFT CG step. The preconditioned direction is followed by the CG correction and DFT line minimization. More than 80 systems have been tested, including molecules, bulk hetero structures, defects, surface, molecule absorbed on semiconductor and metal surface, metal clusters, as well as hybrid organic/inorganic systems. This covers most systems used in everyday *ab initio* atomic relaxations. The speed-up ranges from a factor of 2 to a factor of 9. A simple valence force field (VFF) for the covalent bonding part of the system and a general embedded atom method (EAM) for the metallic part of the system are used. Besides the requirement for indicating which part (atoms) is covalent and which part (atoms) is metallic, there is no need to provide any other information. The code and lib are provided in the Supplemental Material [14], which can be used as a plugin in any standard DFT code. We believe the method can be widely adopted for different systems.

Our classical force field Hamiltonian consists of several terms as follows:

$$E_{FF} = E_{\mathrm{vff}} + E_{\mathrm{gupta}} + E_{\mathrm{shift}} + E_{\mathrm{delta}},$$

Here the E_{vff} is a unified valence force field (VFF), which has the following form:

$$E_{\mathrm{vff}} = \sum_{i=1}^{N_{\mathrm{bond}}} k_b (b_i - b_{i0})^2 + \sum_{j=1}^{N_{\mathrm{angle}}} k_a (\theta_j - \theta_{j0})^2,$$

where b_i is the bond length and θ_{j} is the bond angle. What is important is that this E_{vff} is reconstructed at every step of the *ab initio* atomic relaxation $R_0(t)$, b_{i0}, and θ_{j0} are taken from the current bond distance and angle values from the current atomic configuration $R_0(t)$ at this step. Note every bond and angle have their own b_{i0} and θ_{j0} values. These values are not type specific (e.g., different carbon-carbon bond pair can have different, b_{i0}). In another words, at the current step $R_0(t)$, the E_{vff} is zero, and its force term is also zero. Nevertheless, it does provide a Hessian matrix, which contains useful information for the connectivity of the atoms. We have used general parameter for k_b and k_a for all bonds and angles, $k_b = 30\,\mathrm{eV}/\mathrm{\AA}^2$, $k_a = 5\,\mathrm{eV}/\mathrm{rad}^2$, regardless of the atom types. Thus, to construct the above E_{vff}, the only issue is the determination of the nearest-neighbor list. We have used a bond distance cutoff to determine the bonds. This cutoff is taken as the sum of the standard atomic radius, which are provided in Table SI in the Supplemental Material (SM) [14]. Note that there are ionic bond systems where the valence bond topology is not well defined. Nevertheless, we found that the above E_{vff} can still be used in such cases. One can even have different number of bonds due to the use of different bond length cutoffs, but the resulting speed-ups are similar. If two parts of a system are bonded with van der Walls force, there could be no covalent bonding between them. Their relative shift will be described by the E_{shift} term to be discussed later.

While the E_{vff} takes care of the covalent bonded, and even the ionic bonded regions, for metallic region (metal bulk/slab/cluster), one can take advantage of the supreme quality of the embedded atom model (EAM). In particular, we have adopted the Gupta potential [15], which has a form as:

$$E_{\mathrm{gupta}} = \sum_{i=1}^{N} \left\{ \sum_{j\neq i}^{N} A_{ij} \exp\left(-p_{ij}\left(\frac{r_{ij}}{r_{ij}^0} - 1\right)\right) - \left[\sum_{j\neq i}^{N} \xi_{ij}^2 \exp\left(-2q_{ij}\left(\frac{r_{ij}}{r_{ij}^0} - 1\right)\right)\right]^{\frac{1}{2}} \right\},$$

where atom j is the neighbor of atom i within a sufficiently large cutoff, which is 2 times of the bond cutoff used in the E_{VFF}. r_{ij} is the first-neighbor distance in the lattice. A_{ij} and p_{ij} describe the Born-Mayer ion-ion repulsions, ξ_{ij} is the effective hopping distance, and q_{ij} describes its dependence on the relative interatomic distance. There are atomic specific parameters for most common metal elements as described in Refs. [16–20]. The parameters for many A-B metal atom pairs also exists, if they do not exist, a geometry average for the A, q, p, ζ parameters and an algebra average for r^0 of the two end atoms can be used. If the A-A parameter for a given element does not exist, but A1-A1, A2-A2 parameters for the two neighboring elements A1 and A2 (in the periodic table) exist, one can also take the average parameters of A1 and A2 to get an approximated parameter set for A. Some of the existing parameters are listed in Table SII in the SM. Note that one needs to specify, for each atom, whether it belongs to the metallic region, or nonmetallic region. The atom pairs A-B of the above Gupta formula is included only when both A and B belong to the metallic region. While a covalent bond A-B in E_{vff} can exist when at least one atom belongs to the covalent bond region. If there is an aggregation of metallic elements in one place, we suggest assigning them as metal. However, if one metallic element is surrounded by other nonmetallic elements, as in covalent and ionic crystals, or embedded in a molecule or two-dimensional (2D) system, we suggest assigning it as nonmetal. Theoretically, there could be cases where a metallic situation changes to nonmetallic situation, or vice versa. Such cases are usually rare. Even when that happens, with the wrong assignment, the code will still work, although the acceleration might suffer. In the worse scenario when such rare cases happen, one can stop the relaxation, and reassign the metal/nonmetal types.

Besides the above two main force field terms, we have also introduced an absolute shift energy term:

$$E_{\text{shift}} = \sum_i^{N_{\text{atom}}} k_s (R_i - R_{i0})^2.$$

Here R_i is the atomic coordinate, and R_{i0} is taken from the current atomic position R_0(step) at this atomic relaxation step. We have used a general constant $k_s = 1.5\,\text{eV}/\text{Å}$. This term prevents the shift of the system to large distance. It is like having a diagonal term in the Hessian matrix. This is useful to fix the overall shift and rotation of isolated molecules or for cases where two parts are only connected by van der Waals interaction, which is not represented in both the E_{vff} and E_{GUPTA} potential.

Given the above three energy terms (E_{vff}, E_{GUPTA}, E_{shift}), one could calculate the Hessian matrix and use it for the preconditioner of the CG method. However, for large systems, the calculation of such Hessian matrix can be expensive. Besides, we like to update the Hessian matrix as the system evolves, especially if the initial configuration is far away from the local minimum. We also like to go beyond the use of linear information of the Hessian matrix. For example, for metallic cluster, when proper E_{GUPTA} is used, it is found that the E_{GUPTA} can guide the *ab initio* energy line minimization along a curved path, which is better than a plain use of Hessian matrix [8]. We have thus adopted this follow-the-force-field-path approach. In this approach, at each *ab initio* atomic relaxation step, the system will be fully relaxed based on the force field (FF) model constructed at the current step. The force field relaxed atomic positions will then be used for *ab initio* line minimization. This approach, however, requires the force field atomic force at each *ab initio* step R_0(step) to be the same as the DFT force. In our previous works [8,11], this has been achieved by explicit force field fitting at each step. However, the force field based on the above three general formalisms and parameters: $E_{\text{vff}} + E_{\text{GUPTA}} + E_{\text{shift}}$ will not have the same atomic force as the DFT force. The E_{vff} and E_{shift} will have zero force, while the E_{GUPTA} might have a different force. To make the FF force the same as that of the DFT result, we have introduced a linear energy term:

$$E_{\text{delta}} = -\sum_i \Delta F_i(\boldsymbol{R_i} - \boldsymbol{R_{io}}),$$

Where, ΔFi is the force difference between the DFT force and the FF force (using the above three FF terms) evaluated at the current *ab initio* atomic relaxation step R_0(step):

$$\Delta F = \boldsymbol{F}^0_{dft} - \boldsymbol{F}^0_{ff}.$$

The addition of this linear force correction term can make the FF minimum close to the DFT minimum. Figure 1 shows a molecule case for the DFT minimum position, and the FF minimum position with and without the E_{delta} term.

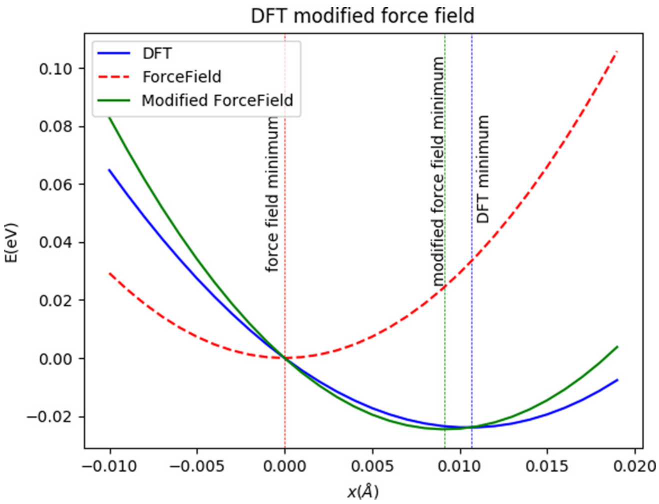

FIG. 1. Energy curvature of DFT, force field, modified force field for the glycine system along the DFT force direction of the initial atomic configuration. This is for glycine system, during one minimization step, x denotes the distance along the FF relaxation direction.

With the E_{FF} set up at each step of the *ab initio* atomic relaxation (before line minimization), we can now use this E_{FF} to guide our DFT line minimization search. The procedure is the following: at each *ab initio* atomic relaxation step k, its atomic coordinates $R_0(k)$ are used to construct $E_{FF}(k)$ following the above procedure. Then the atomic coordinates are relaxed following $E_{FF}(k)$ (this itself can use its own CG method, or BFGS method, it takes negligible amount of time compared to the *ab initio* part of the calculation). After it reached the minimum point $R_{0m}(k)$, we will take $F^p{}_k = R_{0m}(k)$–$R_0(k)$. Note, if everything is in the parabolic energy region, $R_{0m}(k)$–$R_0(k) = M^{-1}F_{DFT}$, where M is the Hessian matrix of the E_{FF}. Thus our method will become a preconditioned CG method in that limit. After the F_k^p is obtained, the CG feature is included by constructing the line searching direction as:

$$\boldsymbol{p}_k = \boldsymbol{F}_k^p + \frac{\boldsymbol{F}_k^p \cdot \boldsymbol{F}_k}{\boldsymbol{F}_{k-1}^p \cdot \boldsymbol{F}_{k-1}} \boldsymbol{p}_{k-1}.$$

An *ab initio* energy line minimization along the direction of p_k will be performed. We have used Brent's method for this line minimization [21]. In most cases, one trial step is sufficient for this line minimization step. The minimum position will be used as the starting point for step $k+1$: $R_0(k+1) = R_0(k) + \alpha p_k$, here α is the step size for this line minimization. The flow chart of the whole PCG procedure is shown below in Fig. 2.

We have tested 82 systems, all the calculations are done using the PWMAT code [22,23], which is a GPU code for plane-wave pseudopotential DFT calculations. SG15 [24,25] norm-conserving pseudopotentials are used. The typical plane-wave energy cutoff is 50 Ryd.

All the 82 systems have reached the DFT force criterion. However, there are a few cases where the PCG found minimum is slightly different from the CG found minimum, actually all with slightly lower energies (e.g., within 0.06 eV or 0.002 eV).). This is more relevant to the cases where the reported speed-up is close to 1. In a way, this is not

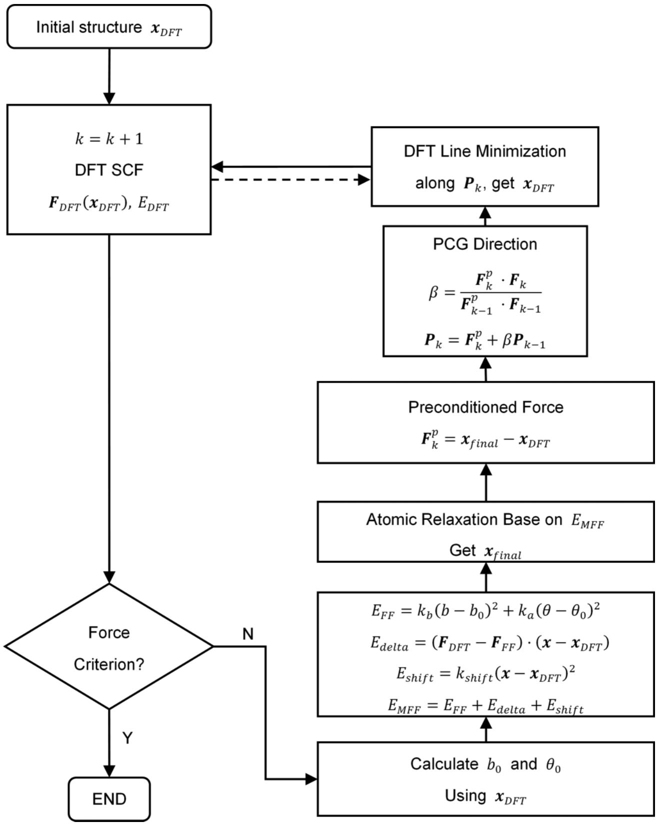

FIG. 2. The flowchart of the force field guided preconditioned conjugate gradient method. Dotted line in the flow chart means that the line minimization contains SCF calculations.

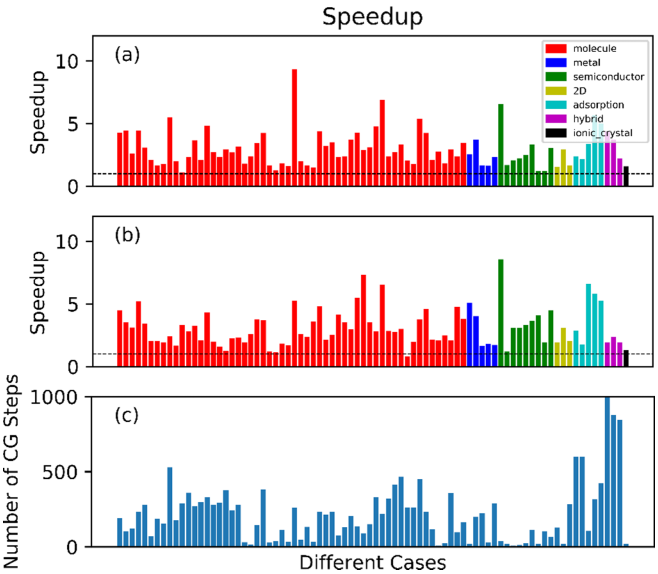

FIG. 3. The speed-up factors for different systems. (a) the speed up measured by the force criterion; (b) the speed up measured by reaching the half energy drop; (c) the CG steps to reach the force criterion without the use of the acceleration method. The types of systems are color coded in (a) and (b).

really the fault of PCG or CG. When there are multiple minima surrounding the initial starting atomic configuration, there is no guarantee different relaxation methods (CG, PCG, BFGS, steepest decent, FIRE, etc.) will reach the same local minimum. One can indeed define a potential basin where the initial atomic position belongs. However, to guarantee to reach the bottom of that basin, steepest decent with very small time steps (no line minimization) need to be used, which is hardly a practice method for atomic relaxation. The relaxation speed-ups for these 82 systems are shown in Fig. 3, along with the relaxation steps needed to converge the system when the preconditioner is not used. These systems have 5–216 atoms with various system types. Organic molecules include carbon chains, amino acids, and benzene rings. Metallic systems include copper cluster, silver cluster, copper surface, nickel-aluminide alloy. Semiconductors include gallium arsenide with vacancies, diamond silicon with vacancies, GaAs-InAs heterostructure. 2D materials include silicene supercell and molecules absorbed on silicene; ionic systems include sodium chloride supercell. All the systems, including their numbers of atoms are listed in Table SIII. We have measured the speed-up in two different ways. One is the number of steps needed to reach the 0.01 eV/A force criterion, another is the number of steps needed for the ΔE (the total energy minus the final minimum energy) to drop to one-half of its original values. The initial atomic positions of these systems are prepared either by universal force field (UFF) [26] relaxation (for the molecular system), or at their ideal crystal positions (for defect, heterostructure), or simply place a molecule on top of a surface. These are the typical initial positions researchers used in their material simulations. For most of the 82 systems, we have a speed-up around 2.0, and some of them have a high accelerating factor up to 9. Without using the acceleration, most of these systems take in the order of 100–200 steps to reach the minimum, while some systems take about a 1000 steps. Thus a factor of 2–3 can mean a significant saving of time.

In the following, we describe these systems in more detail. As listed in Table SIII, simple carbon chains and 20 types of common amino acids are tested. The carbon chains have numbers of atoms ranging from 5 to 62. The amino acids contain common organic atomic types, such as oxygen, nitrogen, sulfur, as well as different bonding topologies: single bonds, double bonds, and rings. The number of atoms for the amino acids ranges from 10 to 26. The initial configurations are obtained by relaxation using AVOGADRO 1.2 [27] with Universal Force Field [26]. Figure 4 shows the relaxation of four amino acids cases. CG cannot converge them in 100 steps, BFGS method gives a slightly better result for some systems, and the new method converges the system in 40–60 steps with an accelerating factor of 2–4 relative to the CG method.

We have tested metallic systems, including clusters, metallic heterojunctions, and metal surface with adsorbed molecule. As discussed before, EAM potential is used to describe the metallic part of the system in our accelerating scheme. Gupta EAM potential is relatively close to DFT potential energy surface, this leads to a good acceleration for the PCG method. We tested the metallic clusters Ag_{55}, Ag_{16}, 128 atom Ni_3Al_Ni metallic alloy, as well as Cu surface with absorbed molecules containing 122 atoms. These are real systems used for cluster

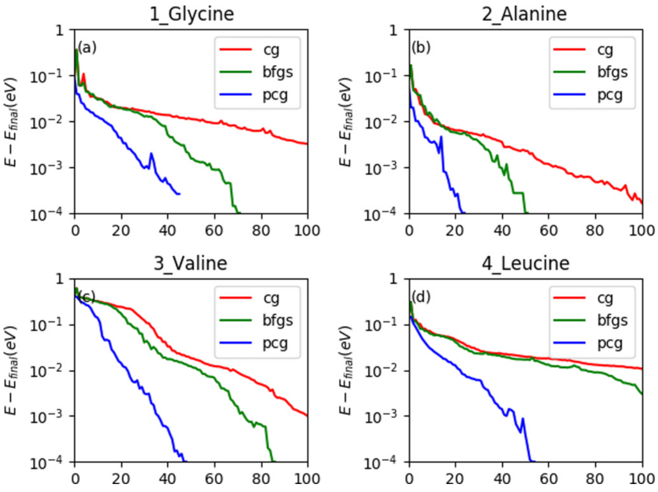

FIG. 4. First 100 relaxation steps for four amino acids for the three methods: CG (conjugated gradient), BFGS, and PCG (the current preconditioned conjugated gradient method). The vertical axis is $\Delta E = E(\text{step}) – E\_\text{final}$ in eV, the horizontal axis is the CG steps.

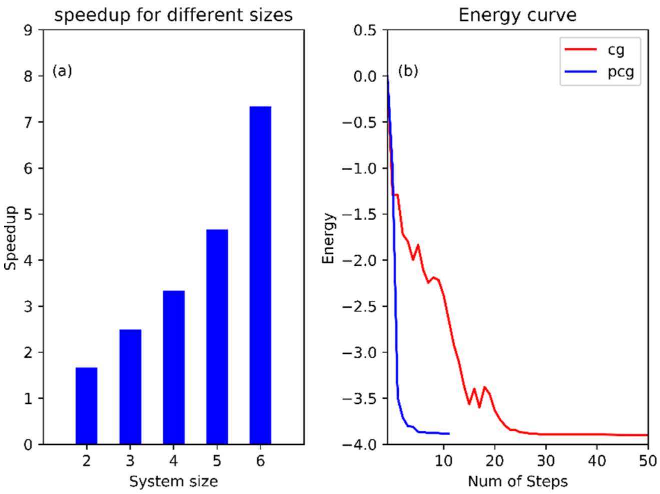

FIG. 5. GaAs-InAs heterostructures. (a) Speed-up factor of different sizes of systems. We construct GaAs supercells from 2 × 1 × 1 to 6 × 1 × 1, replace half or less half of the Ga atoms to In atoms, and randomly move all the atoms by a random shift less than 0.1 Å. (b) Typical energy curve in main accelerate region (6 × 1 × 1).

studies, or metallic catalysis. The speed-ups for these systems are around 2–4.

It is also interesting to test the effects of our method for defects within semiconductors or strained heterojunction systems. To do this, we have taken the bulk GaAs and Si supercells containing 216 atoms, and remove some atoms to form vacancies. The initial structure is the ideal atomic positions of the perfect crystal. We also constructed a CdS-CdSe quantum well as well as a GaAs-InAs quantum well containing 64 atoms with the perfect crystal position using the average lattice constants as our initial atomic configurations. These are the typical mechanical problems for strain relaxation. The PCG method gives a 2–3 speed-up for semiconductors with point defects and a speed-up factor of 3–6 for the relaxation of the strained systems. These are typical problems encountered in defect calculations and nanostructure calculations. As a matter of fact, the larger the system, the higher speed-up is expected in such bulklike systems. This is because for large systems, the soft acoustic phonon modes become lower in energy, which worsens the condition number of the Hessian matrix, and makes the relaxation converge slower. However, our force field model describes well such mechanical acoustic modes, especially for their relationship to their corresponding wave numbers. As a result, the approximated Hessian matrix from the force field model can correct the soft modes through the preconditioning, and restore the speed of the atomic relaxation. To demonstrate this fact systematically, we have now provided the speed-up of a semiconductor bar with increasing bar length in Fig. 5. As one can see, the speed-up increases with the bar length.

We also tested three organic/inorganic hybrid perovskite systems. Such systems (e.g., the methylammonium lead iodide, $MAPbI_3$) have been intensely studied in recent years for solar cell research. However, due to the existence of the organic molecules and their relative weak interaction with the inorganic framework, the atomic relaxations of such systems are quite challenging. In our cases, with about 100 atoms, the original CG method can only converge the systems after 800–1000 steps. Our PCG method can converge the systems within 400 steps. Some of the actual relaxation curves of the above-discussed problems are shown in Fig. 6.

Finally, we have tested a few surface-molecule adsorption cases: a 7 × 7 2D silicene adsorbing one H_2O molecule (total 101 atoms); a 7 × 7 2D silicene adsorbing one SO_2 molecule (total 101 atoms); 6 × 6 2D molybdenum disulfide adsorbing one NH_3 molecule (total 112 atoms); and PbS (001) and (111) surfaces adsorbing one oleic acids molecule [(001) 85 atoms, (111) 105 atoms]. The conventional CG method typically has very slow convergences for these systems due to the possible rotation and other soft configuration changes of the molecule on the substrate. The first three cases give speed-up factors around 3–6. In the case of PbS adsorbing oleic acids cases,

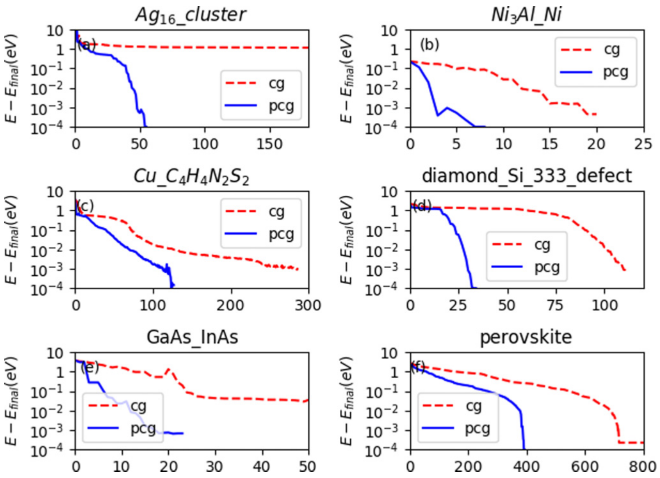

FIG. 6. Relaxation curves of different systems: (a) Ag16 cluster; (b) Ni3AlNi alloy; (c) Molecule C4H4N2S2 on Cu surface; (d) Point defect in bulk Si; (e) GaAs-InAs heterostructure; (f) MAPbS4 hybrid perovskite supercell. The horizontal axis is the CG steps.

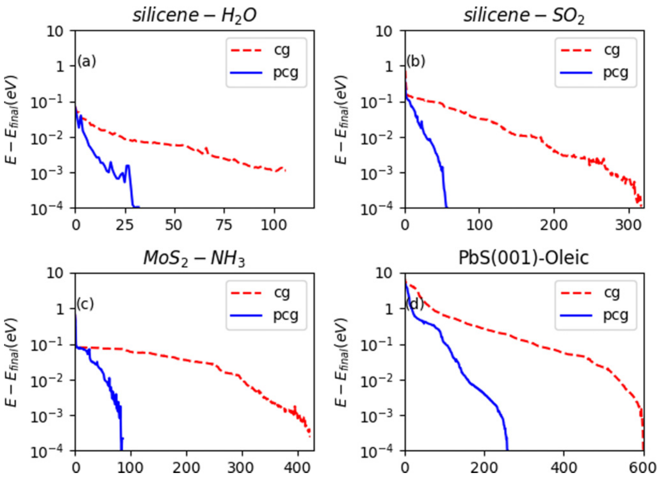

FIG. 7. The actual relaxation curves for systems with one molecule absorbed on a substrate: (a) one water molecule on silicene; (b) one SO2 molecule on silicene; (c) one NH3 molecule on MoS2; (d) An oleic acid molecule on the PbS (001) surface. The horizontal axis is the CG steps.

our PCG method converges in less than 300 steps, while the conventional CG method cannot converge after 1500 steps. The speed-up at half energy is about a factor of 3. A few examples of the actual relaxation curves are shown in Fig. 7.

In summary, we have presented a force field guided DFT PCG method to speed up *ab initio* atomic relaxations. In this method, a simple force field model is constructed at every step of the *ab initio* atomic relaxation. Such a simple force field model allows the application of the current method to all common material simulation problems, providing accelerations to most of the cases we have tested. The force field is constructed in such a way that its atomic forces are the same as that of the DFT forces at each step. The system is then relaxed following the energy of the constructed force field (with negligible amount of computational time). The relaxed position is used as the preconditioning corrected gradient direction for the DFT PCG method. 82 different systems have been tested, covering a wide range of material simulation problems. Across the board, we found the speed-up typically in the range of 2–6. Since *ab initio* atomic relaxation takes a major chunk of the computational time for material simulations, we expect the current method can be widely adopted in many studies. The code and lib for this method are provided in the GitHub [28], which can be used as a plugin in a standard *ab initio* atomic relaxation code. In our future work, an important direction is to develop an efficient automatic method to distinguish the local types of a system in a given region. Another is to determine whether we can consider Coulomb interaction and van de Walls interaction. More systems also need to be tested to fully confirm and understand the potential and limitation of this method. These will provide better force field parameters to make the PCG method more robust and efficient.

This work is supported by the Director, Office of Science (SC), Basic Energy Science (BES), Materials Science and Engineering Division (MSED), of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231 through the Materials Theory program (KC2301). This work is also financially supported by the MOST Project of China (Grant No. 2014CB920903), the NSF of China (Grants No. 11734003, No. 11574029), and International Graduate Exchange Program of Beijing Institute of Technology. We used the resources of National Energy Research Scientific Computing center (NERSC) located in Lawrence Berkeley National Laboratory.

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[28] See the static lib at https://github.com/llpjaj/DFT_PCG_atomic_relaxation.