A Periodic Genetic Algorithm with Real-Space Representation for Crystal Structure and Polymorph Prediction

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A novel Genetic Algorithm is described that is suitable for determining the global minimum energy configurations of crystal structures and which can also be used as a polymorph search technique. This algorithm requires no prior assumptions about unit cell size, shape or symmetry, nor about the ionic configuration within the unit cell. This therefore enables true ab initio crystal structure and polymorph prediction. Our new algorithm uses a real-space representation of the population members, and makes use of a novel periodic cut for the crossover operation. Results on large Lennard-Jones systems with FCC- and HCP-commensurate cells show robust convergence to the bulk structure from a random initial assignment and an ability to successfully discriminate between competing low enthalpy configurations. Results from an ab initio carbon polymorph search show the spontaneous emergence of both Lonsdaleite and graphite like structures.

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I. INTRODUCTION

The prediction of crystal structures from first principles has long been recognized as one of the outstanding challenges in solid state physics. The most recent methods of cluster expansion assume the lattice structure of the crystal. Good results for silicon have been shown using minima hopping, but this method assumed the number of atoms and unit cell of the structures searched. In this communication we demonstrate a new method for unbiased ab initio crystal structure determination using a novel Genetic Algorithm which makes no assumptions of atom number, unit cell or lattice structure.

Genetic Algorithms (GAs) were first developed by John Holland in 1975, and are stochastic global optimization methods based on “survival of the fittest”. This is a computational technique which is used to solve problems in which there are many potential solutions, only a small number of which are optimal. We initialize our system with a number of random candidate solutions which are grouped together into a population, with each solution being a member of this population. There needs to be a way of determining the fitness of each member, i.e. some way of telling which members are better or worse solutions to the problem than the other members. It is this fitness function which defines the problem. Population members will be chosen or selected, based on their fitness, to become parents to produce offspring in a breeding procedure known as crossover. Crossover involves creating one or more offspring which are a combination of features from their parents. Each population member needs to be encoded or represented in some way such that crossover can be performed in a systematic way. For example, in the case of binary strings, two parents, 11010011 and 01011001 may be split in half and recombined to make two new offspring 11011001 and 01010011. The offspring may be mutated after crossover, which involves making changes to offspring in a random way which could introduce beneficial aspects into the population. In the binary string case this most often involves changing a small percentage of the bits on the string. Using each member’s fitness the population is updated by only allowing some population members to survive into the next generation, the rest of the population members will be discarded. The original formulation used a binary string representation, which is described in detail in Holland. In this study the problem is the determination of the optimal configuration of atoms, where the fitness function is a function of the enthalpy of the system.

GAs were not widely used in the field of solid state physics due to the representation issue, the binary nature of which was insufficient to describe the complicated atomic and molecular systems that are of interest. This changed in 1995 when Deaven and Ho described a GA technique for clusters using a representation which used the atomic coordinates of the systems being studied. Crossover was performed by taking a planar cut through the center of each parent and swapping halves to generate offspring. After crossover the resulting structures of the resulting population members may be a long way from equilibrium and so a quasi-Newton minimizer is used to relax each structure to the minimum of the local basin of attraction. This reduces the problem by simplifying the po-
tential energy surface that is searched by the GA. This method shows excellent convergence for a number of complicated systems, and recently studies of nanowires and surfaces have been performed using a similar technique. The cluster calculations are performed using non-periodic codes, but the nanowire and surface studies make use of periodic boundary conditions (PBCs) in either one or two dimensions, and a planar cut does not take these PBCs into account. Bulk binary-encoded GA studies have been presented by Woodley and real-space encoded studies of bulk molecular crystals have been reported by Harris et al in which crossover was performed by randomly swapping of groups of parameters between population members, rather than considering the structural configuration of the atoms within the crystal.

In this article, we demonstrate that for periodic GA studies using a periodic cut in the crossover operation is superior to a planar one. The periodic cut is chosen to have the same periodicity as the supercell of the population member, and this reduces the discontinuities produced in the offspring operation, which would cause extra work for the local minimizer that is required in the GA scheme. Results show that a periodic cut has a faster convergence than a planar one for large systems. We also apply this technique to systems where the unit cell of the solution is optimized as well as the atomic coordinates. Finally we show that GAs are suitable as a polymorph search technique.

II. METHOD

The crossover is performed in fractional coordinates, as described in figure 1. The cut is defined by any periodic function with the same periodicity as the cell, \( f \left( \mathbf{s}_{\text{atom}}^{(\zeta, \eta)} \right) \), where \( \mathbf{s}_{\text{atom}}^{(\zeta, \eta)} \) is the fractional position vector for each atom along the \( (\zeta, \eta) \) = (a, b), (b, c) or (c, a) directions. This function gives a vector (in fractional coordinates) \( \mathbf{s}_{\text{cut}} \) for each \( \mathbf{s}_{\text{atom}} \) in the population member. The metric tensor \( \mathbf{a} = \mathbf{h} \mathbf{h} \) where \( \mathbf{h} = [a, b, c] \) (in Cartesian coordinates), is used to calculate the product

\[
\alpha_{\text{cut}} = (\mathbf{s}_{\text{cut}} - \mathbf{s}_{\text{atom}})^T \mathbf{q} \mathbf{X}
\]

where \( \mathbf{X} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \) in fractional coordinates (\( \mathbf{X} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \)) and with the criterion

\[
\alpha_{\text{cut}} = \begin{cases} > 0 & \text{the atom is "above" (outside) the cut} \\ \leq 0 & \text{the atom is "below" (inside) the cut.} \end{cases}
\]

As the cut is made in fractional coordinates, it does not "know" about the Cartesian shape of the cell, so this technique allows two population members with different cells to be bred during crossover, rather than being constrained to both parents having the same supercell. The technique also allows the cell size and shape to be evolved along with the crystal structure.

Figure 2 shows the crossover operation where two cuts are required in the cell. Every crossover operation performed has an equal probability of being calculated with the cuts made in reference to either the a, b or c directions. This ensures that none of the three co-ordinate directions is preferred over the other two, but also allows large areas of each of the population members to be undisturbed by the cut. To ensure that no one parent is preferred over the other, the center of each of the cuts should be made one-quarter and three-quarters up the chosen cell axis which gives approximately even mixing.

In the Deaven and Ho formulation, the plane of the cut was defined by the creation of a random unit vector on the surface of a sphere which was centered on the center of mass of the cluster. In our method cuts made in different cell directions can have different random wavelengths and amplitudes, although a maximum amplitude should be defined so that the cut is contained within the simulation supercell, and obviously the wavelength of the cut cannot be longer than twice the cell vector in that direction, whilst any cut with a wavelength of less than half the atomic separation will appear as a flat plane.

Fitness is determined by the relative enthalpy per atom of the population members, and each population member was chosen for crossover based on its fitness using roulette wheel selection. Similar to Chuang et al., the number of atoms in each individual population member can be varied by accepting all solutions after crossover, or if the number of atoms needs to be constrained then solutions are rejected until offspring are generated that have the correct number.

Roulette wheel selection can also be used in the update procedure, which determines which members of the original population should progress through to the next generation. In ad-
dition, the lowest energy population member was guaranteed to be selected for update when updating by this method. By allowing some higher energy members to remain, this update procedure prevents the population from becoming stagnated.

An alternative method for updating is to only allow the lowest M population members to proceed to the next generation, from a super-population of 2M parents and offspring. We will refer to this method as the “simple” update scheme.

The way that mutation is performed is also important. This is controlled by two quantities, mR and mA. The mutation rate is mR ∈ [0, 1], and this determines the probability that each atom will be mutated or not after crossover, before the local structure minimization procedure. Once an atom has been selected for mutation then it is randomly placed in a cubic box with sides of length 2mA which has been centered on the atom’s original position.

\[
V_{SF}(r_{ij}) = \begin{cases} 
  V_{LJ}(r_{ij}) - V_{LJ}(r_{cut}) - \left( \frac{dV_{LJ}(r_{ij})}{dr_{ij}} \right)_{r_{ij}=r_{cut}} (r_{ij} - r_{cut}) & r_{ij} \leq r_{cut} \\
  0 & r_{ij} > r_{cut}
\end{cases}
\]

which has a HCP ground state structure\textsuperscript{12} which is almost degenerate with the FCC structure (energy difference from HCP +0.1\%\textsuperscript{13}. The energy difference between the FCC and HCP supercells used in this study was +0.072\%, due to the above formulation of the Lennard-Jones potential. The value of \( \sigma \) was set to 3.405 Å, \( \epsilon \) was set to 120 K, and \( r_{cut} \) was set to 2.5\( \sigma \). While the ground states are very close in energy, to switch from FCC to HCP four out of every six layers require a stacking fault.

For the Lennard-Jones results we used a fixed supercell, but allowed the number of atoms to either be fixed for each of the population members, or be allowed to vary. We compared GA minimization calculations using either the planar or periodic cuts as described above. The number of population members was fixed at \( M = 16 \), and the initial number of atoms in each population member was set to \( N = 150 \) using a hexagonal supercell, which is commensurate with perfect FCC and HCP structures without stacking faults. The mutation rate, \( m_R \), was set to 0.10 (10\%) and the mutation amplitude, \( m_A \), was set to 2.5Å. The initial configuration of the population members is totally randomized, then minimized with the local minimizer before proceeding. A total of 200 generations was run for each simulation.

In total 15 simulations were performed from a random start for each of the eight combinations of either fixed or variable number of atoms, using either the roulette wheel or simple update scheme, and with crossover performed using either periodic cuts or a planar cut. A summary of the convergence times is shown in figure\textsuperscript{15}.

III. RESULTS

A. Results from the Empirical Lennard-Jones potential

All calculations were performed by adding the above GA formulation to the \textit{ab initio} planewave DFT code CASTEP\textsuperscript{14} which has also been modified for ease of algorithm testing to allow the use of the empirical Lennard-Jones potential\textsuperscript{15}

\[
V_{LJ}(r_{ij}) = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6}
\]

in the shifted-force formulation\textsuperscript{16}.

1. Empirical Lennard-Jones bulk studies with a fixed number of atoms.

For these studies the number of atoms was kept fixed at 150 during the whole of the simulation. However, none of the 60 calculations resulted in minimization down to FCC or HCP stacking. The simple update scheme was much faster at reach-
with 150 atoms and a local minimum enthalpy

FIG. 4: Typical results from a 150 atom (variable), 16 population member calculation starting from an initial random configuration with a mutation rate of 10% and mutation amplitude of 2.5Å, using roulette wheel selection in the update procedure. Periodic cuts were used and the system converged in 29 generations to a structure with 150 atoms and a local minimum enthalpy +0.024 % above the HCP minimum.

...ing convergence, and using periodic cuts was much faster than using a planar cut when using either update scheme.

2. Empirical Lennard-Jones bulk studies with a variable number of atoms.

Results from Chuang et al. showed that allowing the number of atoms to vary helped convergence. Our results also show this. The use of periodic cuts using the roulette wheel update scheme, or the planar cut using the roulette wheel or simple update scheme, allowed the system to be minimized to a defect-free ground state structure. Periodic cuts were faster to convergence than a planar cut, as shown above.

We found that the system did not converge into a perfect lattice structure without allowing for variable atom number. Figure 4 shows a typical set of results, using periodic cuts with roulette wheel selection for update. In this case the system converged in 29 generations to the structure shown in figure 5. This configuration is an FCC-HCP hybrid with an energy difference of +0.024 % from the HCP ground state, which is due to a single FCC plane stacking fault. Similar structures were also found using a planar cut, but with longer convergence times.

B. Ab initio carbon polymorph studies with a variable supercell.

An interesting alternative application of our GA is in the field of polymorph prediction. For example, there has been considerable interest recently in carbon polymorphs. Systematic ab initio searches have been made of sp$^3$-hybridized structures with four atoms per unit cell and of sp$^2$-hybridized structures with four or six atoms per unit cell.

Such calculations either require a graph-theoretical enumeration of possible configurations, resulting in an exponentially growing search space as the number of atoms per unit cell increases, or serendipity. By contrast, our GA approach is not restricted to any particular form of bonding or chemical intuition, and is very efficient at searching high dimensional spaces. As an application of our GA to polymorph determination we therefore chose to study the four atom per unit cell carbon polymorphs.

All calculations were performed using density functional theory (DFT) to treat the electrons for a given configuration of ions so no assumptions were made about the nature of the underlying bonding. DFT has been shown to be very accurate for the calculation of atomic configurations many times - for general reviews see Payne et al. or Segall et al. For the results shown a planewave basis set was used to represent the wavefunction, with a 400 eV cutoff and 0.05 Å$^{-1}$ sampling of reciprocal space using the Monkhorst-Pack scheme. Non-local ultrasoft pseudopotentials were used to describe the electron-ion interaction and the local density approximation (LDA) was used to treat exchange correlation effects. The LDA was used in preference to the various generalized gradient approximation (GGA) functionals, as these are known to underbind weakly interacting systems such as graphite sheets. The positions of the ions and the unit cell vectors were simultaneously optimized using the quasi-Newton method of Pfrommer et al., with the reciprocal space sampling density and effective planewave cutoff energy maintained at all times.

Only update by roulette wheel selection is used when performing a polymorph search to allow a large amount of variation in the cell bond lengths and angles, and in the ionic positions. Out of 8 population members which had all been randomly initialized, at the end of the tenth generation there were five which had a graphite-like character and three which had a Lonsdaleite character. A summary of these results, compared with diamond, graphite and Lonsdaleite, is shown in table I. Structure 1 is shown in more detail in figure 6. Within the LDA the binding between graphene sheets in graphite is only very weakly dependent on the alignment of the sheets, and thus any alignment is permissible, as seen in the differences

FIG. 5: Side view of minimized structure from figure 4, looking down the [011] direction. The colors show the mixture of FCC (gray) and HCP (black) stacking.
of alignment between figure 5 and figure 7 which shows structure 5. Figure 8 shows structure 7 which is Lonsdaleite. Since this is a snapshot of the population after 10 generations, any configurations of ions are possible, and so diamond structures need not be expected. We are currently optimizing the algorithm and the values of the parameters in order to generate as wide a range of structures as possible and results will be presented in a forthcoming publication.

IV. CONCLUSIONS

We have demonstrated a general method for first principles determination of crystal structures using a genetic algorithm in a periodic supercell. This technique exploits the inherent periodicity in the system in the calculation of crossover between parent members of the population by using a periodic cut in the crossover operation. This shows much faster convergence when compared to crossover performed using a planar cut, as used in lower dimensional studies.

There are a number of advantages to this method. First, by performing all crossovers in fractional co-ordinates each population member may be allowed to have unit cells which have different sizes and shapes, and if the local minimizer also optimizes the cell vectors then the optimization process will not be biased by choice of initial structure. Indeed, we always start from an initial random structure so there is no initial bias to any preconceived solution. Secondly, we also suggest that the roulette selection method could be used as a polymorph search technique, since this does not force the population down into a single basin, but allows the search space to be continually explored. Future work will include further ab initio studies using a variable number of atoms and the application of this method to surfaces. A systematic study of the ab initio carbon polymorphs with the genetic algorithm discussed is still in progress and will be presented in a forthcoming publication.

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| Structure     | Categorization | Bond Lengths   |
|---------------|----------------|----------------|
| Diamond       | -              | 1.52672 Å      |
|               |                | 1.52672 Å      |
| Graphite      | -              | 1.40731 Å      |
|               |                | 1.40731 Å      |
| Lonsdaleite   | -              | 1.52244 Å      |
|               |                | 1.54583 Å      |
| 1             | Graphite-like  | 1.40696 Å      |
| 2             | Lonsdaleite-like| 1.52241 Å   |
|               |                | 1.54583 Å      |
| 3             | Graphite-like  | 1.40679 Å      |
| 4             | Graphite-like  | 1.40707 Å      |
| 5             | Graphite-like  | 1.40701 Å      |
| 6             | Lonsdaleite-like| 1.52225 Å   |
|               |                | 1.54602 Å      |
| 7             | Lonsdaleite-like| 1.52225 Å   |
|               |                | 1.54599 Å      |
| 8             | Graphite-like  | 1.40736 Å      |

TABLE I: Summary of the eight carbon structures found in polymorph search compared with diamond, graphite and Lonsdaleite.
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1. J. Maddox, Nature 335, 201 (1988).
2. A. VanDewalle, Nature Materials 4, 362 (2005).
3. V. Blum, G. L. W. Hart, M. J. Walorski, and A. Zunger, Phys. Rev. B 72, 165113 (2005).
4. G. L. W. Hart, V. Blum, M. J. Walorski, and A. Zunger, Nature Materials 4, 391 (2005).
5. S. Goedecker, J. Chem. Phys 120, 9911 (2004).
6. J. H. Holland, Adaptation in Natural and Artificial Systems (MIT Press/Bradford Books Edition, 1992), ISBN 0-262-58111-6.
7. D. M. Deaven and K. M. Ho, Phys. Rev. Lett. 75, 288 (1995).
8. R. L. Johnston, Dalton Trans. 4193 (2003).
9. B. L. Wang, S. Y. Yin, G. H. Wang, A. Buldum, and J. J. Zhao, Phys. Rev. Lett. 86, 2046 (2001).
10. F. C. Chuang, C. V. Ciobanu, V. B. Shenoy, C. Z. Wang, and K. M. Ho, Surf. Sci. 573, L375 (2004).
11. F. C. Chuang, C. V. Ciobanu, C. Predescu, C. Z. Wang, and K. M. Ho, Surf. Sci. 578, 183 (2005).
12. S. M. Woodley, Struct. Bonding (Berlin) 110, 95 (2004).
13. K. D. M. Harris, S. Habershon, E. Y. Cheung, and R. L. Johnston, Z. Kristallogr. 219, 838 (2004).
14. M. D. Segall, P. L. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. Payne, J. Phys.: Cond. Matt. 14, 2717 (2002).
15. J. E. Lennard-Jones and A. E. Ingham, Proc. Royal Soc. A107, 636 (1925).
16. S. D. Stoddard and J. Ford, Phys. Rev. A 8, 1504 (1973).
17. G. L. Pollack, Rev. Mod. Phys. 36, 748 (1964).
18. G. Kane and M. Goeppert-Mayer, J. Chem. Phys 8, 642 (1940).
19. R. T. Strong, C. J. Pickard, V. Milman, G. Thimm, and B. Winkler, Phys. Rev. B 70, 045101 (2004).
20. B. Winkler, C. J. Pickard, V. Milman, and G. Thimm, Chem. Phys. Lett. 337, 36 (2001).
21. B. Winkler, C. J. Pickard, V. Milman, W. E. Klee, and G. Thimm, Chem. Phys. Lett. 312, 536 (1999).
22. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992).
23. H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
24. J. D. Pack and H. J. Monkhorst, Phys. Rev. B 16, 1748 (1977).
25. D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
26. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
27. B. G. Pfrommer, M. Cote, S. G. Louie, and M. L. Cohen, J. Comp. Phys. 131, 233 (1997).
28. N. L. Abraham and M. I. J. Probert, a genetic algorithm based ab initio study of carbon polymorphs, (in preparation).