A redundant internal coordinate algorithm for optimization of periodic systems

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The algorithm for optimizing molecular geometries in redundant internal coordinates is extended to periodic systems. The lattice vectors are not explicitly included in the set of optimized coordinates, but are adjusted only implicitly via a combination of chemically meaningful inter- and intracell internal coordinates. The Wilson B matrix required for coordinate transformations is modified to include internal coordinate derivatives with respect to lattice vectors. The efficiency of the algorithm is demonstrated on a one-dimensional polymer, poly(*p*-phenylenevinylene), and a three-dimensional crystal of urea. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1340578]

I. INTRODUCTION

Geometry optimization has become an almost mandatory step in computational studies of individual molecules.[1] Much attention has been devoted to making optimizations reliable and efficient. Newton–Raphson methods are perhaps the most rapidly convergent, but they require the computation of second derivatives or Hessians at each step in the optimization.[2] However, for most levels of theory, second derivatives are significantly more difficult to calculate than gradients (first derivatives), and their computation scales poorly with the size of the system. Consequently, quasi-Newton techniques have emerged as the method of choice since they use only gradients.[2] These algorithms start with a crude estimate of the Hessian and improve it during the course of the optimization by using a variety of possible updating methods.

It has also become clear that internal coordinates are more efficient than Cartesians for optimizing molecular systems.[1] Redundant internal coordinates are especially useful for polycyclic molecules and other highly connected systems.[3] Such coordinate systems are constructed from the stretches, bends, and torsions involving all of the bonded atoms in a molecule. Thus, the coordinate system automatically reflects the chemical connectivity and takes into account the inherent curvilinear nature of internal motions of molecules. A well-chosen internal coordinate system has much less coupling between coordinates than a Cartesian coordinate system, allowing the optimized structure to be found in significantly fewer steps. Furthermore, a diagonal estimate of the Hessian is often sufficient for rapid and reliable convergence of the optimization.[4] Traditional methods for transforming between Cartesian and internal coordinates scale as $O(N^3)$ with system size. However, with recent developments, this transformation can be carried out with $O(N^2)$ effort and even $O(N)$ when sparse matrix techniques are used.[5] When combined with $O(N)$ methods[6] for electronic structure calculations, this permits systems as large as plasminogen (1226 atoms) to be optimized readily on workstations.[7]

To the best of our knowledge, optimizations of periodic systems carried out to date utilized either fractional or Cartesian coordinate systems. Structural studies with electronic structure methods have been performed mostly for highly symmetric systems with few independent degrees of freedom (typically 1–10), so the efficiency of the optimizer has not been a big issue. Furthermore, in most of these cases analytic energy gradients were not available, thus limiting the size of the system being studied. On the other hand, in periodic molecular mechanics calculations, energy, forces, and even exact Hessians are relatively inexpensive computationally, so high optimization efficiency can be achieved by combining the readily available exact Hessian with a simple fractional or Cartesian coordinate based method.[8] When optimizing the unit cell parameters, orientation-related instabilities can occur if one does not take account of the three rotational degrees of freedom present in the nine Cartesian components of the lattice vectors. To overcome such problems the variable-cell-shape algorithm[9] employs six dot products of the lattice vectors instead of their individual Cartesian components. In another approach,[8] minimization of the unit cell energy at constant pressure is carried out via the strain matrix containing six unique components, also removing the rotational degrees of freedom from the optimization.

In the present work, we describe an alternative and potentially superior approach that uses redundant internal coordinates to implicitly optimize the lattice vectors of a periodic system. Because periodic structures have connectivities that are similar to cyclic and cage-like molecules, one can anticipate that redundant internal coordinates will be the best choice in this case as well. Our tests demonstrate that when redundant internal coordinates are used, the number of steps

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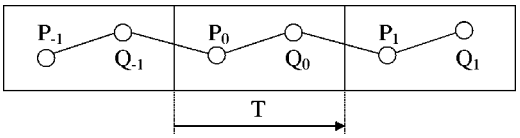

FIG. 1. A two-atomic periodic chain.

required to optimize a periodic system is similar to that required for a comparable molecular system (i.e., one made out of the unit cell of the periodic system). This number is also small in absolute terms, thus confirming the high efficiency of our redundant internal coordinate algorithm, which uses only a simple diagonal guess for the Hessian matrix.

II. METHOD

One of our main goals in using redundant internal coordinates for periodic systems is to employ chemically meaningful coordinates such as bond lengths, valence angles, and dihedral angles to represent not only the positions of atoms within a unit cell, but also the relative orientation and spacing between atoms in adjacent unit cells. Thus, changes in the internal coordinates can also adjust the lattice vectors. For example, consider a planar, one dimensional chain, $-[P_{-1}-Q_{-1}]-[P_0-Q_0]-[P_1-Q_1]-$ (Fig. 1). If one optimizes the bond length within a unit cell P_0-Q_0, the bond length spanning adjacent cells Q_0-P_1, and the angles $P_0-Q_0-P_1$ and $Q_0-P_1-Q_1$, then the translation vector T will be optimized implicitly as a combination of these bonds and angles. Force constants or Hessian matrix elements for these internal coordinates should be comparable to those for isolated molecules, and similar initial estimates can be used.[4] These force constants implicitly provide estimates for the Hessian matrix elements for the lattice vectors and their coupling with the other coordinates, which might be rather difficult to estimate otherwise.

An optimization algorithm employing internal coordinates requires a transformation matrix between Cartesian displacements and internal coordinate displacements. In molecular calculations, this is the well-known Wilson B matrix,[10] originally used in vibrational analysis. The B matrix for periodic systems is here defined similarly

$$\delta\mathbf{q}=\mathbf{B}\delta\mathbf{r}, \tag{1}$$

where $\mathbf{q}=(q_1,q_2,\ldots,q_m)^T$, $\mathbf{r}=(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n,\mathbf{t}_1,\mathbf{t}_2,\mathbf{t}_3)^T$, and $B^a_{i,j}=\partial q_i/\partial r^a_j$. The $\mathbf{r}_i=(r^x_i,r^y_i,r^z_i)$ are the absolute positions of the atoms within the central cell, and $\mathbf{t}_i=(t^x_i,t^y_i,t^z_i)$ are the lattice vectors. Accordingly, the derivatives of the energy with respect to the lattice vectors (stress tensor) should be calculated with the absolute atomic positions within the cell fixed; we have referred to this quantity as the solid cell stress in our previous work.[11]

In the periodic case, there are two types of internal coordinates—intracell and intercell. Intracell coordinates allow one to adjust the relative positions of atoms within the unit cell. Therefore, the periodic B matrix elements for intracell coordinates are computed exactly in the same way as in a comparable molecule. Intercell coordinates span two or more cells and depend on atomic coordinates in cells other than the central cell (cell 0). Yet, periodic systems are completely defined by the coordinates in cell 0 and the translational vectors. Coordinates of atoms in other cells can be readily obtained by an appropriate translation. Therefore, intercell coordinates effectively depend on atomic positions within the central cell and translational vectors. Optimization of such coordinates results in the adjustment of atomic positions and translational vectors, without considering the latter explicitly. A rather straightforward way to obtain the periodic B matrix for intercell coordinates is then the following. First, by treating all atoms within a given internal coordinate as independent, one computes the molecular B matrix components for each atom using the usual formulas.[10] Next, by applying the chain rule, these molecular B matrix elements are transformed into periodic ones. Several examples presented in the following should clarify this procedure.

In the above-mentioned example (Fig. 1), the system is defined via the vector $\mathbf{r}=(\mathbf{P}_0,\mathbf{Q}_0,\mathbf{t})$, where $\mathbf{P}_0=(P^x_0,P^y_0,P^z_0)$, $\mathbf{Q}_0=(Q^x_0,Q^y_0,Q^z_0)$, and $\mathbf{t}=(t^x,t^y,t^z)$. In the following, we represent the molecularlike B matrix components as $\hat{B}$, which are the partial derivatives of internal coordinates with respect to the explicit atomic positions. The periodic B matrix elements required for our optimization method are total derivatives of a given internal coordinate with respect to an atomic position in cell 0, and the lattice vectors. To simplify notation, we denote the total derivative of a given internal coordinate q_i with respect to the Cartesian component a of atomic position $\mathbf{P}_0$ as

$$B^a_{i,P}\equiv B^a_{i,P_0}=\frac{dq_i}{dP^a_0}. \tag{2}$$

For intracell coordinates, such as P_0-Q_0, the periodic B matrix elements are identical to the molecular ones ($\hat{B}$) because all the atoms are located within cell 0 and therefore the corresponding total and partial derivatives are the same. Denoting the P_0-Q_0 bond length as $q_i=q(\mathbf{P}_0,\mathbf{Q}_0)$, one obtains

$$B^a_{i,P}=\frac{dq_i}{dP^a_0}=\frac{\partial q_i}{\partial P^a_0}=\hat{B}^a_{i,P_0},\quad B^a_{i,Q}=\frac{dq_i}{dQ^a_0}=\frac{\partial q_i}{\partial Q^a_0}=\hat{B}^a_{i,Q_0}. \tag{3}$$

For the intercell case, e.g., the Q_0-P_1 bond, some additional manipulations are necessary to obtain the total derivatives with respect to atoms within the central cell and the lattice vectors. Let $q_j=q(\mathbf{Q}_0,\mathbf{P}_1)$ be the intercell bond Q_0-P_1. First, the molecular B matrix elements for Q^a_0 and P^a_1 are calculated as

$$\hat{B}^a_{j,Q_0}=\frac{\partial q_j}{\partial Q^a_0},\quad \hat{B}^a_{j,P_1}=\frac{\partial q_j}{\partial P^a_1}. \tag{4}$$

Using $P^a_1=P^a_0+t^a$, the required total derivatives with respect to P^a_0 and t^a are then obtained as

$$B^a_{j,P}=\frac{dq_j}{dP^a_0}=\frac{\partial q_j}{\partial P^a_1}\cdot\frac{\partial P^a_1}{\partial P^a_0}=\frac{\partial q_j}{\partial P^a_1}=\hat{B}^a_{j,P_1}, \tag{5}$$

$$B^a_{j,t}=\frac{dq_j}{dt^a}=\frac{\partial q_j}{\partial P^a_1}\cdot\frac{\partial P^a_1}{\partial t^a}=\frac{\partial q_j}{\partial P^a_1}=\hat{B}^a_{j,P_1}, \tag{6}$$

where we have used that

$$\frac{\partial P_1^a}{\partial P_0^a}=1, \quad \frac{\partial P_1^a}{\partial t^a}=1. \tag{7}$$

For the angle $Q_0-P_1-Q_1$, denoted as $q_k=q(\mathbf{Q}_0,\mathbf{P}_1,\mathbf{Q}_1)$, the periodic B matrix elements are

$$B_{k,Q}^a=\frac{dq_k}{dQ_0^a}=\frac{\partial q_k}{\partial Q_0^a}+\frac{\partial q_k}{\partial Q_1^a}\cdot\frac{\partial Q_1^a}{\partial Q_0^a}=\hat{B}_{k,Q_0}^a+\hat{B}_{k,Q_1}^a, \tag{8}$$

$$B_{k,t}^a=\frac{dq_k}{dt^a}=\frac{\partial q_k}{\partial P_1^a}\cdot\frac{\partial P_1^a}{\partial t^a}+\frac{\partial q_k}{\partial Q_1^a}\cdot\frac{\partial Q_1^a}{\partial t^a}=\hat{B}_{k,P_1}^a+\hat{B}_{k,Q_1}^a. \tag{9}$$

The last example illustrates that for intercell internal coordinates depending on more than one atom in an adjacent cell or the same atom appearing in more than one cell, the corresponding periodic B matrix elements have contributions from more than one molecular $\hat{B}$ matrix element. We also note that because of simple expressions describing atomic coordinates in cells other than cell 0 through coordinates in cell 0 and translational vectors, any periodic B matrix element is at most a sum of molecular contributions $\hat{B}$, such as in the previously mentioned q_k.

It is also instructive to consider the bond P_0-P_1. Let $q_l=q(\mathbf{P}_0,\mathbf{P}_1)$ and recall that the molecular $\hat{B}$ matrix elements are translationally invariant (i.e., $\hat{B}_{l,P_0}^a+\hat{B}_{l,P_1}^a=0$ in the present case), then

$$B_{l,P}^a=\frac{dq_l}{dP_0^a}=\frac{\partial q_l}{\partial P_0^a}+\frac{\partial q_l}{\partial P_1^a}\cdot\frac{\partial P_1^a}{\partial P_0^a}=\hat{B}_{l,P_0}^a+\hat{B}_{l,P_1}^a=0, \tag{10}$$

$$B_{l,t}^a=\frac{dq_l}{dt^a}=\frac{\partial q_l}{\partial P_1^a}\cdot\frac{\partial P_1^a}{\partial t^a}=\hat{B}_{l,P_1}^a. \tag{11}$$

The only surviving B component is for the lattice vector, as it should be. On the other hand, the bond $q_m=q(\mathbf{P}_1,\mathbf{Q}_1)$ will contribute to the following periodic B matrix elements:

$$B_{m,P}^a=\frac{dq_m}{dP_0^a}=\frac{\partial q_m}{\partial P_1^a}\cdot\frac{\partial P_1^a}{\partial P_0^a}=\hat{B}_{j,P_1}^a, \tag{12}$$

$$B_{m,Q}^a=\frac{dq_m}{dQ_0^a}=\frac{\partial q_m}{\partial Q_1^a}\cdot\frac{\partial Q_1^a}{\partial Q_0^a}=\hat{B}_{j,Q_1}^a, \tag{13}$$

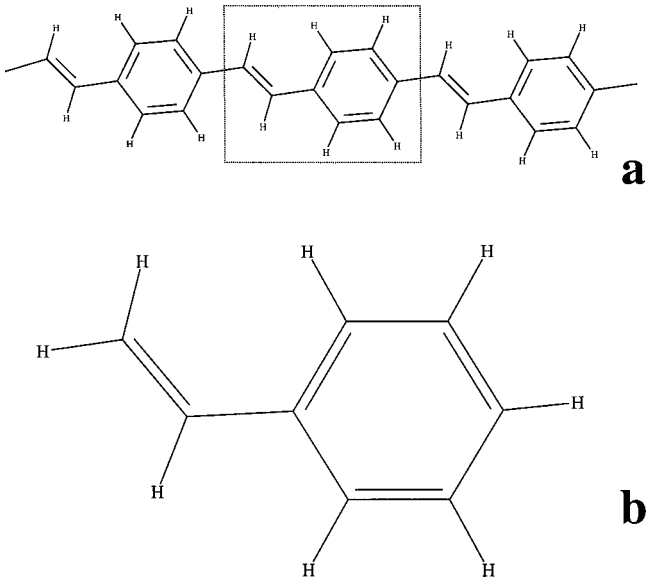

FIG. 2. (a) Poly(*p*-phenylenevinylene). (b) Styrene.

$$B_{m,t}^a=\frac{dq_l}{dt^a}=\frac{\partial q_m}{\partial P_1^a}\cdot\frac{\partial P_1^a}{\partial t^a}+\frac{\partial q_m}{\partial Q_1^a}\cdot\frac{\partial Q_1^a}{\partial t^a}=\hat{B}_{m,P_1}^a+\hat{B}_{m,Q_1}^a=0, \tag{14}$$

where the last result is again due to the translational invariance of the molecular B matrix elements. As expected, the bond $q(\mathbf{P}_1,\mathbf{Q}_1)$ does not depend on the translational vector and yields the same B matrix contributions as the bond $q(\mathbf{P}_0,\mathbf{Q}_0)$. Consequently, an arbitrary translation of all atoms in a given internal coordinate will lead to a coordinate identical to the original one.

In a general three-dimensional periodic system, intracell bonds will be of the type $P(0,0,0)-Q(0,0,0)$, while the intercell bonds are of the type $P(c_1,c_2,c_3)-Q(d_1,d_2,d_3)$, where all of the c_a and d_b indices are either 0 or 1. As a consequence, a given coordinate will contribute to lattice vectors $\mathbf{t}_i$ when c_i or d_i are 1. For example, the bond $P(0,0,0)-Q(1,1,1)$ will have nonzero periodic B matrix elements for atoms P and Q, and all three lattice vectors. Similar considerations apply to angles and dihedrals. To generate a full set of intra- and intercell internal coordinates, one can replicate the central cell and obtain a $2\times2\times2$ cluster of cells with cell indices 0 and 1. Then, all of the possible bonds, angles, and dihedrals are generated within this cluster and

TABLE I. Comparison of optimizations of periodic and molecular systems. E denotes energy (in a.u.), $\sqrt{\Sigma F^2}$—RMS_Force (in a.u.), $\sqrt{\Sigma \Delta x^2}$—RMS_Displacement (in a.u.).

	PPV polymer— $[C_8H_6]_\infty$			Styrene molecule—C_8H_8		
Cycle	$E(\Delta E)$	$\sqrt{\Sigma F^2}$	$\sqrt{\Sigma \Delta x^2}$	$E(\Delta E)$	$\sqrt{\Sigma F^2}$	$\sqrt{\Sigma \Delta x^2}$
1	−306.353 871 9	0.010 74	0.169 48	−307.526 000 6	0.008 08	0.192 20
2	(−0.012 176 9)	0.004 46	0.055 79	(−0.006 698 0)	0.002 98	0.072 83
3	(−0.002 523 9)	0.001 88	0.004 21	(−0.001 873 9)	0.001 32	0.005 12
4	(−0.000 094 5)	0.000 62	0.000 86	(−0.000 086 0)	0.000 34	0.000 91
5	(−0.000 009 5)	0.000 14	0.000 15	(−0.000 006 5)	0.000 07	0.000 28
	−306.368 676 7			−307.534 665 0		

TABLE II. Convergence of the PPV polymer optimization. E denotes energy (in a.u.), T—translational vector (in Å), dE/dT—force (in a.u.).

	$[(C_8H_6)_1]_\infty$			$[(C_8H_6)_2]_\infty$		
Cycle	$E(\Delta E)$	$T(\Delta T)$	dE/dT	$\frac{1}{2}\cdot E(\Delta E)$	$\frac{1}{2}\cdot T(\Delta T)$	dE/dT
1	−306.353 871 9	6.4485	0.034 97	−306.353 871 9	6.4485	0.034 97
2	(−0.012 176 9)	(0.3871)	−0.014 02	(−0.013 256 8)	(0.3497)	−0.011 23
3	(−0.002 523 9)	(−0.1191)	−0.002 10	(−0.001 468 8)	(−0.0811)	−0.002 01
4	(−0.000 094 5)	(−0.0014)	−0.000 79	(−0.000 072 0)	(−0.0029)	−0.000 62
5	(−0.000 009 5)	(−0.0007)	−0.000 14	(−0.000 007 3)	(0.0001)	−0.000 13
	−306.368 676 7	6.7142		−306.368 676 9	6.7143	

duplicate ones are thrown away by applying translational invariance. For example, bond $P(0,1,1)-Q(1,0,1)$ is the same as $P(0,1,0)-Q(1,0,0)$ and is eliminated. A similar approach is used for valence angles and dihedrals.

With this method, optimization of periodic systems requires only minor modifications to an algorithm for redundant internal coordinate optimization of molecules. Details of our molecular optimization algorithm have been described previously.[3(d),5(a),5(b)] Since all of the machinery commonly used for molecular optimizations is available, it can be used in novel ways for periodic cases. For example, if the lattice vector $\mathbf{t}_1$ is to be held constant, one simply freezes the distance $P(0,0,0)-P(1,0,0)$. Similarly, to freeze the angle between lattice vectors $\mathbf{t}_2$ and $\mathbf{t}_3$, one can constrain the angle $P(0,1,0)-P(0,0,0)-P(0,0,1)$; to keep the $P-Q$ bond at a given angle to the $\mathbf{t}_1$ lattice vector, one would constrain $P(0,0,0)-Q(0,0,0)-Q(1,0,0)$. Therefore, in our method one can use the existing capabilities for applying constraints if it is desired to freeze some or all of the lattice parameters.

III. EXAMPLES

All calculations were carried out with the GAUSSIAN[12] suite of programs extended for calculations on periodic systems as described in Ref. 11. The computational method used here for illustration purposes is the PBE density functional for exchange and correlation[13] together with a 3-21G basis set. The optimization thresholds were Max_Force =0.00045, RMS_Force=0.0003, Max_Displacement =0.0018, RMS_Displacement=0.0012, all in atomic units. The optimization was stopped when all these conditions were satisfied. This particular set of values corresponds to the default convergence criteria in the GAUSSIAN package.[12]

First, we analyze the optimization of a one-dimensional polymer, poly(*p*-phenylenevinylene) $[C_8H_6]_\infty$ (PPV) [Fig. 2(a)]. The initial geometry was chosen as C–H bond=1.09 Å, C–C aromatic bond=1.39 Å, C–C double bond=1.36 Å, conjugated C–C single bond=1.44 Å, and all valence angles =120°. All atoms lay within a plane, so the dihedrals are either 0° or 180°. The **k** space integration employed 16 points. For comparison, we also optimized a molecule structurally similar to the unit cell of PPV–styrene C_8H_8 [Fig. 2(b)]. Its initial geometrical parameters (bonds and angles) were set to values identical to those in the PPV case. A simple valence force field was employed for the initial guess of the force constants, which is the default for optimizations in GAUSSIAN. The optimization convergence pattern for both structures is shown in Table I. It is evident that for these structures the two procedures perform similarly, confirming that optimization of the periodic system in internal coordinates is just as efficient as in the nonperiodic case. The molecular framework in both systems is relatively rigid, and a minimum is found in just five cycles. In PPV, the internal coordinate selection algorithm defined 15 bonds, 24 valence angles, and 36 dihedrals, totaling 75 coordinates, compared to 39 nonredundant degrees of freedom.

It is instructive to compare the optimization of PPV using one and two (C_8H_6) polymer units per cell. Table II lists energies at each step, translational vectors, and the derivative of the energy with respect to this vector. For comparison purposes, the energies and translational vector for the larger unit cell are scaled by 1/2. While for the doubled unit cell the translational vector is twice that for a single unit cell, the derivative dE/dT is the same in both cases. This is because in our definition of dE/dT only one bond is affected by dT,[11(a)] and it is the same bond in both cases [the bond crossed by the cell box in Fig. 2(a)]. Overall, both optimizations proceed similarly, the small differences found are probably caused by slightly different force constant matrices with the redundant degrees of freedom projected out.

We also optimized urea in its $P\bar{4}2_1m$ crystal phase at zero pressure. This is a highly symmetric system, with each

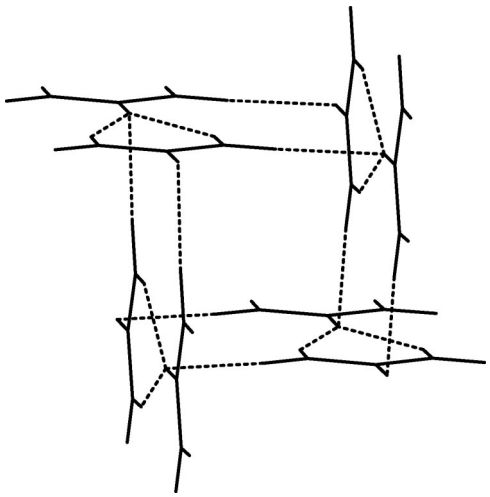

FIG. 3. A fragment of the urea crystal. The four molecules shown in front define the simulation cell used in this work.

TABLE III. Convergence of the urea optimization. The three translational vectors are $[T_1, T_2, T_2]$. E denotes energy (in a.u.), $\sqrt{\Sigma F^2}$—RMS_Force (in a.u.), $\sqrt{\Sigma \Delta x^2}$—RMS_Displacement (in a.u.).

T_2 step	$E(\Delta E)$	$\sqrt{\Sigma F^2}$	$\sqrt{\Sigma \Delta x^2}$	T_1	T_2
1	−895.300 319 0	0.015 04	0.026 73	4.684	7.870
2	(−0.016 220 5)	0.005 83	0.014 00	4.710	7.902
3	(−0.003 932 0)	0.003 36	0.045 35	4.673	7.863
4	(−0.005 065 1)	0.001 94	0.021 23	4.587	7.736
5	(−0.000 554 2)	0.001 78	0.004 59	4.558	7.679
6	(−0.000 220 1)	0.000 89	0.007 96	4.563	7.670
7	(0.000 003 9)	0.000 48	0.004 81	4.565	7.646
8	(−0.000 033 2)	0.000 51	0.002 47	4.564	7.660
9	(−0.000 065 1)	0.000 19	0.000 98	4.572	7.661
10	(−0.000 005 6)	0.000 14	0.003 54	4.572	7.659
11	(−0.000 005 8)	0.000 08	0.002 07	4.575	7.653
12	(−0.000 007 7)	0.000 06	0.000 50	4.574	7.659
	−895.326 424 3				

urea molecule NH_2CONH_2 occupying a site of C_{2v} symmetry. Currently our program is capable of utilizing only limited symmetry—the point group of the unit cell. Therefore, in our calculations we use a unit cell with 4 urea molecules (32 atoms), and the point group of the unit cell was constrained to be S_4 (Fig. 3). During the optimization, atomic displacements are symmetrized via the operations of the unit cell point group. We have also frozen all dihedral angles to further reduce the actual number of degrees of freedom being optimized. The purpose of this procedure is to avoid numerical noise present in the forces and to ensure symmetry of the final structure. We used a $2\times2\times4$ mesh of **k** points for the reciprocal space integration. The atoms in the unit cell have 99 degrees of freedom; however, the number of independent degrees of freedom is actually much smaller. The optimization employed 204 redundant internal coordinates, including 36 bonds, 24 hydrogen bonds, 48 angles, 16 linear angles, and 80 dihedrals. The optimization convergence pattern starting from the experimental geometry found in Ref. 14 (also used in Ref. 15) is shown in Table III. In the early stages of the optimization the lattice vectors and energy change substantially indicating that the ''strong'' intramolecular coordinates are being brought to their optimum values. In later steps the energy changes are significantly smaller, with a slower decrease in the rms force. Molecules in solid urea are bound by weak hydrogen bonds with relatively shallow minima, and finding a local minimum is more demanding than optimizing covalent distances and angles. Such behavior is not uncommon in weakly bonded systems.

The optimization algorithm described in this work was also recently used to optimize fluorinated carbon nanotubes of C_2F stoichiometry[16] and polyglycines in various conformations, some of which were helices bound by weak hydrogen bonds.[17,18] Overall, a general ''black box'' redundant internal coordinate optimization algorithm such as the one developed here is a very useful tool in structural studies of periodic systems.

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