An efficient internal coordinate method for optimization of periodic structures

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We present an efficient, robust algorithm for optimizing the structures of periodic systems using delocalized internal coordinates. Our method builds on recent advances in optimization methods developed for molecular systems due to Pulay, Baker and others. The high coordination of atoms in typical solid-state systems can lead to enormous numbers of primitive internal coordinates. Special techniques are developed which enables such systems to be handled using internal coordinates.

We go on to present a number important extensions of the internal coordinate optimization methods. Firstly, we develop an approach for combining internal coordinate optimization with Cartesian constraints. This extension can be extremely useful for studies of surfaces where it is often desirable to freeze the atomic position of one or more layers of atoms. Secondly, we show that by adding carefully selected extra coordinates to the optimization space it is possible to perform internal coordinate optimization on systems where the internal coordinates do not span the optimization space. Typically internal coordinates will fail to span the space when there are disconnected fragments in the unit cell and this second development is particularly important in the treatment of systems such as molecular crystals.

A series of application examples of our method are presented on polymers, molecular crystals, zeolites and semiconductor and catalyst surfaces. It is demonstrated that optimizations with delocalized internal coordinates for solid-state systems can be much more efficient than the usual methods based on Cartesian coordinates.