Symmetries and the Hessian

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We have a relaxed structure for our system with atoms at positions $\{r_j^0\}$ where $j = 1, \ldots, N_{at}$ labels the atoms and the r_j^0 are 3-vectors. The relaxed structure has a set of symmetries, and each is given by some 3×3 orthogonal matrix R. The question is how to use the symmetry to reduce the amount of work needed to calculate the Hessian matrix for this structure.

Since we're at a minimum, the total energy has the series

$$E(\{r_j^0 + \delta r_j\}) = E(\{\delta r_j\}) = E_0 + \frac{1}{2}\sum_{i,j} \delta r_i^T H_{i,j} \delta r_j + \cdots$$

where the Hessian matrix H has been represented by its 3×3 subblocks $H_{i,j}$ between atoms i and j. Ignoring this series expansion for the moment, the fact that we have symmetry means that

$$E(\{R\delta r_{R^{-1}j}\} = E(\{\delta r_j\})\,.$$

We have used a shorthand notation above: the 3×3 matrix R acts on one of the δr as matrix-vector multiplication, while $R^{-1}j$ means we are mapping the index of the atom j to the atom index to which it would be mapped to under R^{-1} in space. Basically, what we are saying is that if we rotate the displacement pattern by R and move the atoms accordingly, the energy won't change.

Using this in the Taylor series gives

$$\begin{aligned}
\sum_{i,j} \delta r_i^T H_{i,j} \delta r_j &= \sum_{i,j} (R\delta r_{R^{-1}i})^T H_{i,j} (R\delta r_{R^{-1}j}) \\
&= \sum_{i,j} \delta r_{R^{-1}i}^T (R^T H_{i,j} R) \delta r_{R^{-1}j} \\
&= \sum_{i,j} \delta r_i^T (R^T H_{Ri,Rj} R) \delta r_j
\end{aligned}$$

so we end up with

$$H_{i,j} = R^T H_{Ri,Rj} R$$

or equivalently

$$H_{R^{-1}i,R^{-1}j} = R^T H_{i,j} R\,. \tag{1}$$

This relation can be used as follows. First, we calculate entire columns of the Hessian for a subset of columns j ranging only over the inequivalent atoms (by symmetry): e.g. for a nanotube where we take a sheet unit cell and repeat it around the circumference, j ranges over the atoms of the sheet's primitive cell. So we have $H_{i,j}$ tabulated for all i and a subset of j. We then repeatedly use symmetries R to find the other columns $R^{-1}j$ using the above rule to fill the entire Hessian matrix.