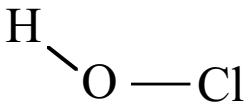
Examples of an Optimization Scheme
HOCl → TS → HClO

Finding the HOCl Minima



Initial guess: r(OH)=1.818 a_o; r(ClO)=3.197 a_o; θ=102.8º

SCF/cc-pVDZ gradients and Hessian (a.u. & radians) :

$$\mathbf{g}_i = \begin{bmatrix} 0.0047 \\ 0.0129 \\ -0.0040 \end{bmatrix} \qquad \mathbf{H}_i = \begin{bmatrix} 0.2904 & -0.0101 & 0.0609 \\ -0.0101 & 0.5582 & -0.0034 \\ 0.0609 & -0.0034 & 0.2161 \end{bmatrix}$$

r(ClO)

r(OH)

θ(HOCl)

The Newton-Raphson step is defined by:

$$\Delta\mathbf{R} = -\mathbf{H}^{-1}\,\mathbf{g} = \begin{bmatrix} -0.022 \\ -0.023 \\ 0.024 \end{bmatrix}$$

The steepest descent step is defined by:

$$\Delta\mathbf{R} = -\,\mathbf{g}$$ (see above)

Note the difference using curvature info makes

Diagonalization of the initial Hessian

Eigenvalues: $\begin{bmatrix} 0.559 \\ 0.324 \\ 0.182 \end{bmatrix}$

Eigenvectors: $\begin{bmatrix} -0.042 & 0.871 & -0.490 \\ 0.999 & 0.045 & -0.005 \\ -0.017 & 0.490 & 0.872 \end{bmatrix}$ r(ClO) / r(OH) / θ(HOCl)

(nth column of the eigenvector matrix corresponds to the nth eigenvalue)

After optimization to the HOCl minimum: r(OH)=1.795 a_o; r(ClO)=3.176 a_o; θ=104.2°

$\mathbf{g} = \begin{bmatrix} 0.0 \\ 0.0 \\ 0.0 \end{bmatrix}$ $\mathbf{H} = \begin{bmatrix} 0.3056 & -0.0107 & 0.0601 \\ -0.0107 & 0.6053 & -0.0034 \\ 0.0601 & -0.00339 & 0.2146 \end{bmatrix}$

Diagonalization of the final Hessian (sorry, the order changed):

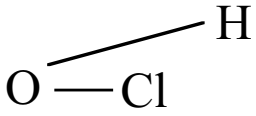
Eigenvalues: $\begin{bmatrix} 0.335 \\ 0.185 \\ 0.606 \end{bmatrix}$

Eigenvectors: $\begin{bmatrix} 0.894 & -0.445 & -0.039 \\ 0.041 & -0.004 & 0.999 \\ 0.445 & 0.895 & -0.015 \end{bmatrix}$

Note: these are not related to the vibrational frequencies since we have not scaled by the masses

At the optimized HClO minimum: r(OH)=4.599 a_O; r(ClO)=3.470 a_O; θ=31.1°

$$\mathbf{H} = \begin{bmatrix} 0.0417 & -0.0481 & -0.1765 \\ -0.0481 & 0.1688 & 0.7747 \\ -0.1765 & 0.7747 & 4.3661 \end{bmatrix}$$



Diagonalization of the Hessian:

Eigenvalues: $\begin{bmatrix} 0.016 \\ 0.049 \\ 4.512 \end{bmatrix}$

Eigenvectors: $\begin{bmatrix} 0.663 & 0.747 & -0.041 \\ 0.741 & -0.648 & 0.176 \\ -0.105 & 0.147 & 0.984 \end{bmatrix}$

r(ClO)
r(OH)
θ(HOCl)

relatively large eigenvalue indicates a large sensitivity for changes in this coordinate

In HClO coordinates: r(HCl)=2.423 a_O; r(ClO)=3.470 a_O; θ=101.1°

Diagonalization of the Hessian:

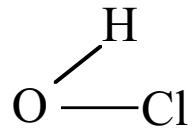
Eigenvalues: $\begin{bmatrix} 0.357 \\ 0.025 \\ 0.112 \end{bmatrix}$

Eigenvectors: $\begin{bmatrix} 0.016 & 0.975 & 0.220 \\ 1.000 & -0.021 & 0.017 \\ -0.022 & -0.220 & 0.975 \end{bmatrix}$

r(ClO)
r(HCl)
θ(HClO)

Optimization to the isomerization transition state

Initial guess geometry: r(OH)=3.067 a_o; r(ClO)=3.318 a_o; θ(HOCl)=44.9º



Initial gradient and Hessian:

$$\mathbf{g}_i = \begin{bmatrix} -0.0392 \\ -0.0131 \\ 0.0166 \end{bmatrix} \qquad \mathbf{H}_i = \begin{bmatrix} 0.1490 & 0.0997 & 0.3311 \\ 0.0997 & 0.0134 & 0.4407 \\ 0.3311 & 0.4407 & 2.5583 \end{bmatrix}$$

Note that it's certainly not obvious that the initial Hessian has the correct form

After diagonalization, however (i.e., a new coordinate system):

Eigenvalues: $\begin{bmatrix} -0.071 \\ 0.113 \\ 2.679 \end{bmatrix}$ Eigenvectors: $\begin{bmatrix} -0.238 & 0.962 & 0.134 \\ 0.962 & 0.215 & 0.167 \\ -0.131 & -0.169 & 0.977 \end{bmatrix}$

Now, one sees that we do indeed have the correct number of negative eigenvalues

Optimizing to the TS

Newton-Raphson step in internal coordinates:

$$\Delta\mathbf{R} = -\mathbf{H}^{-1}\,\mathbf{g} = \begin{bmatrix} 0.386 \\ 0.008 \\ -0.058 \end{bmatrix} \begin{matrix} r(ClO) \\ r(OH) \\ \theta(HOCl) \end{matrix}$$

i.e., stretch the ClO & OH distances and contract the angle

Or analogously in the coordinates that diagonalized the Hessian: $\Delta\mathbf{R} = \sum_{k=1}^{3} -\frac{\mathbf{v}_k^T \mathbf{g}\, \mathbf{v}_k}{\lambda_k}$

where $\mathbf{v}_k$ is the kth column of the eigenvector matrix and λ_k is the associated eigenvalue

This results in a walk uphill along the reaction path (along the gradient, $\lambda_k<0$)
and downhill along the other coordinates orthogonal to the path
(in directions opposite to their gradients, $\lambda_k>0$).