2.9: Linear Triatomic Molecule

Here is an interesting problem. It should be straightforward to calculate the rotational inertia of the above molecule with respect to an axis perpendicular to the molecule and passing through the center of mass. In practice it is quite easy to *measure* the rotational inertia very precisely from the spacing between the lines in a molecular band in the infrared region of the spectrum.

If you know the three masses (which you do if you know the atoms that make up the molecule) can you calculate the two interatomic spacings x and y ? That would require determining two unknown quantities, x and y, from a single measurement of the rotational inertia, I. Evidently that cannot be done; a second measurement is required. Can you suggest what might be done? We shall answer that shortly. In the meantime, it is an exercise to show that the rotational inertia is given by

$$ax^2+2hxy+by^2+c=0, \tag{2.9.1}$$

where

$$a=m_1(m_2+m_3)/M \tag{2.9.2}$$

$$h=m_1m_3/M \tag{2.9.3}$$

$$b=m_3(m_1+m_2)/M \tag{2.9.4}$$

$$M=m_1+m_2+m_3 \tag{2.9.4}$$

$$c=-I \tag{2.9.5}$$

Example 2.9.1: OCS

Suppose the molecule is the linear molecule OCS, and the three masses are 16, 12 and 32 respectively, and, from infrared spectroscopy, it is determined that the moment of inertia is 20. (For this hypothetical illustrative example, I am not concerning myself with units). In that case, equation 2.9.1 becomes

$$11.7\bar{3}x^2+17.0\bar{6}xy+14.9\bar{3}y^2-20=0. \tag{2.9.6}$$

We need another equation to solve for x and y. What can be done chemically is to prepare an isotopically-substituted molecule (isotopomer) such as ^{18}OCS, and measure *its* moment of inertia from its spectrum, making the probably very justified assumption that the interatomic distances are unaffected by the isotopic substitution. This results in a second equation:

$$a'x^2+2h'xy+b'y^2+c'=0. \tag{2.9.7}$$

Let's suppose that the new moment of inertia is $I'=21$, and I leave it to the reader to work out the numerical values of a', h' and b' with the stern caution to retain all the decimal places on your calculator. That is, do not round off the numbers until the very end of the calculation.

You now have two equations, 2.9.1 and 2.9.7, to solve for x and y. These are two simultaneous quadratic equations, and it may be that some guidance in solving them would be helpful. I have three suggestions.

1. Treat equation 2.9.1 as a quadratic equation in x and solve it for x in terms of y. Then substitute this in equation 2.9.7. I expect you will *very* soon become bored with this method and will want to try something a little less tedious.
2. You have two equations of the form $S(x,y)=0$, $S'(x,y)=0$. There are standard ways of solving these iteratively by an extension of the Newton-Raphson process. This is described, for example, in Section 1.9 of my **Celestial Mechanics** notes, and this general method for two or more nonlinear equations should be known by anyone who expects to engage in much numerical calculation.

For this particular case, the detailed procedure would be as follows. This is an iterative method, and it is first necessary to make a guess at the solutions for x and y. The guesses need not be particularly good. That done, compute the following six quantities:

$$S=x(ax+2hy)+by^2+c$$

$$S' = x(a'x + 2h'y) + b'y^2 + c'$$
$$S_x = 2(ax + hy)$$
$$S_y = 2(hx + by)$$
$$S'_x = 2(a'x + h'y)$$
$$S'_y = 2(h'x + b'y)$$

Here the subscripts denote the partial derivatives. Now if

$$x \text{ (true)} = x \text{ (guess)} + \epsilon$$

and

$$y \text{ (true)} = y \text{ (guess)} + \eta$$

the errors ϵ and η can be found from the solution of

$$S_x\epsilon + S_y\eta + S = 0$$

and

$$S'_x\epsilon + S'_y\eta + S' = 0$$

If we calculate

$$F = \frac{1}{S_yS'_x - S_xS'_y}$$

The solutions for the errors are

$$\epsilon = F(S'_yS - S_yS')$$
$$\eta = F(S_xS' - S'_xS)$$

This will enable a better guess to be made, and the procedure can be repeated until the errors are as small as desired. Generally only a very few iterations are required. If this is not the case, a programming mistake is indicated.

3. While method 2 can be used for any nonlinear simultaneous equations, in this particular case we have two simultaneous quadratic equations, and a little familiarity with conic sections provides a rather nice method.

Thus, if $S = 0$ and $S' = 0$ are equations 2.9.1 and 2.9.7 respectively. Each of these equations represents a conic section, and they intersect at four points. We wish to find the point of intersection that lies in the all-positive quadrant - i.e. with x and y both positive. Since the two conic sections are very similar, in order to calculate where they intersect it is necessary to calculate with great accuracy. Therefore, do not round off the numbers until the very end of the calculation. Form the equation $c'S - cS' = 0$. This is also a quadratic equation representing a conic section passing through the four points. Furthermore, it has no constant term, and it therefore represents the two straight lines that pass through the four points. The equation can be factorized into two linear terms, $\alpha\beta - 0$, where $\alpha = 0$ and $\beta = 0$ are the two straight lines. Choose the one with positive slope and solve it with $S = 0$ or with $S' = 0$ (or with both, as a check against arithmetic mistakes) to find x and y. In this case, the solutions are $x = 0.2529, y = 1.000$