# ROTATIONAL MOTION OF LINEAR MOLECULES

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In a previous article (CCP5 Newsletter Number 2, September 1981) I described a simple algorithm for the rotational motion of rigid polyatomic molecules, based on a quaternion representation of the orientation.

The four quaternion parameters are related by a single constraint equation and provide a suitable representation for the orientation of non-linear molecules which have three degrees of rotational freedom. They are less suitable for use with linear molecules which have only two degrees of rotational freedom, as there would then be a second implicit constraint which numerical errors might violate. For these molecules I prefer an algorithm which represents the orientation of the molecule by the cartesian components of a vector along its axis, with a constraint on its length. I learned this algorithm from Konrad Singer, and several other people have used it, but I do not think the details have appeared in print. Furthermore the formulation given below makes clear two points that are not always realised; the algorithms can give the correct dynamics for any linear molecule, not just diatomics and the forcecentres need not necessarily correspond with the mass centres. The discussion below concerns only the rotational motion which of course can be handled completely independently of the translational motion.

We specify the orientation of the molecule by $\underline{e}$, a unit vector along its axis. Let its moment of inertia about a perpendicular axis through the centre of mass be I. If the force centres are at positions $d_\alpha \underline{e}$ relative to the COM the torque on the molecule is:

$$\underline{T} = \underline{e} \times \sum_\alpha d_\alpha \underline{f}_\alpha$$

We study the rotational motion by applying the method of constraints to an 'equivalent diatomic pseudo-molecule'. Let the pseudo-molecule have unit length with masses m at each end on which forces $\underline{G}$ and $-\underline{G}$ act. Its rotational motion will be the same as that of the actual linear molecule provided it has the same moment of inertia and the same torque acts upon it. These conditions are satisfied if:

$$m = 2I$$

and

$$\underline{G} = \sum_\alpha d_\alpha \underline{f}_\alpha - \underline{e}\,(\underline{e}\cdot\sum_\alpha d_\alpha \underline{f}_\alpha)$$

The second term here subtracts out the component parallel to $\underline{e}$, which is irrelevant to the rotational motion. It is not essential but convenient to do this since then $\underline{G}^2 = \underline{T}^2$ and we can obtain the mean square torque which is a useful number to get out of a simulation.

If a and b are the two 'atoms' of the pseudo-molecule they move under the influence of the forces $\underline{G}$ and of undetermined bond forces acting along the axis of the molecule. Applying the leapfrog algorithm to this motion gives:

$$\underline{r}_a^{n+1} = \underline{r}_a^n + \Delta t \dot{\underline{r}}_a^{\,n-\frac{1}{2}} + (\Delta t^2/2I)\ \underline{G}^n + \tfrac{1}{2}\lambda\underline{e}^n$$

$$\underline{r}_b^{n+1} = \underline{r}_b^n + \Delta t \dot{\underline{r}}_b^{\,n-\frac{1}{2}} - (\Delta t^2/2I)\ \underline{G}^n - \tfrac{1}{2}\lambda\underline{e}^n$$

or, since $\underline{e} = \underline{r}_a - \underline{r}_b$

$$\underline{e}^{n+1} = \underline{e}^n + \Delta t\ \dot{\underline{e}}^{n-\frac{1}{2}} + (\Delta t^2/I)\ \underline{G}^n + \lambda\underline{e}^n$$

$$= \hat{\underline{e}} + \lambda\underline{e}^n$$

where $\hat{\underline{e}}$ is the axis vector which would result from 'free-flight' alone. The multiplier $\lambda$ is determined by the condition that the length of the axis must be preserved:

$$\text{i.e.}\quad 1 = |\underline{e}^{n+1}|^2$$

$$= |\underline{e}|^2 + 2\ \lambda\ \underline{e}\cdot\underline{e}^n + \lambda^2|\underline{e}^n|^2$$

giving, remembering that $|\underline{e}^n|^2 = 1$,

$$\lambda = -\ \underline{e}\cdot\underline{e}^n + \left[(\underline{e}\cdot\underline{e}^n)^2 - \underline{e}^2 + 1\right]^{\frac{1}{2}}$$

The algorithm is completed by calculating the new axis vector velocity:

$$\dot{\underline{e}}^{n+\frac{1}{2}} = (\underline{e}^{n+1} - \underline{e}^{n})/\Delta t$$