

# Challenges in Chemistry: Physics/Mechanics 1. challenge

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## 1 Opgaven

1. Formuler på baggrund af den efterfølgende tekst (et udklip fra Peter F. Bernath: Spectra of Atoms and Molecules, 2 Ed.) med egne ord den klassiske mekaniske teori for rotation af molekyler herunder de nødvendige matematiske trin, og definitioner af angulær moment, intertimitomenter og rotationel energi. (NB se nedenstående bemærkning om notationsforbehold)

2. Betragt et plant molekyle. Antag at vi har valgt  $x, y, z$  akser således at intertimitensoren er diagonal, og der gælder at  $I_{zz}$  er større end  $I_{xx}$  og  $I_{yy}$ . Vis at det gælder at  $I_{zz} = I_{xx} + I_{yy}$ .

3. Udregn intertimitoment tensor for følgende molekyler i enheder af  $u\text{\AA}^2$ . Hint: vælg 3 vinkelrette akser, der så vidt muligt følger "symmetriakser" i molekylet. Vælg nu en akse til at være vinkelret på dette plan. Så vil ud-af-diagonal elementer mellem akse vinkelret på planet og akse i planet være nul.

A.  $\text{H}_2\text{S}$  (bindings længde og vinkel: 1.328, 92.2)

B.  $\text{BF}_3$  (bindings længde: 1.307, Vinkler:  $\angle \text{FBF} = 120$ , molekylet er plant). Akse ud af planet igennem B er naturlig principal akse, kaldet  $z$ . Vælg  $x$  langs en (vilkårlig) BF binding, og  $y$  vinkelret på denne.

C. Ethylene,  $\text{C}_2\text{H}_4$ . De interne koordinater er givet som:  $R_{CC} = 1.339$ .  $R_{CH} = 1.086$ ,  $\angle \text{HCH} = 117.6$ ,  $\angle \text{HCC} = 121.2$ .

## 2 Bemærkninger og lidt om matricer

Der er lavet lidt om på jeres matematik og fysik kurser og det har ændret notation nogle steder og nogle emner er skubbet til senere. Hvis der er problemer med at forstå opgaven så giv mig et praj.

Om krydsprodukter se: <http://www.webmatematik.dk/lektioner/matematik-a/vektorer-i-3d/krydsprodukt>

En ting jeg ved har ændret sig er kendskab til matricer. En matrix (flertal matricer) er en kasse af elementer, typisk tal ordnet efter rækker og søjler. Dvs  $\mathbf{A}$  nedenfor er en matrix med to rækker og 2 søjler. Altså en 2 gange 2 matrix. Første række er  $(A_{11} A_{12})$  er første række for eksempel. I en ofte anvendt notation er selve matricen bold imens elementerne er standard (scalarer).

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \quad (1)$$

Der er en masse spændende matematik med matricer og baggrunden bag. En del af det får i lineære transformation på andet år. Vi skal blot bruge nogle enkle fakta om matricer for at forstå at nogle af de trin Bernath skriver op er skrevet op i en smart kompakt notation med matricer. Det er en af de ting matricer kan.

Bemærk at en vektor er en speciel slags matrix. Vi kan tale om en søjle vektor eller en række vektor. Det er eksemplificeret nedenfor med søjle vektoren  $\mathbf{v}$  (en 2 gange 1 matrix) og rækkevektoren  $\mathbf{u}$  (en 1 gange 2 matrix).

$$\mathbf{v} = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} \quad (2)$$

$$\mathbf{u} = ( u_1 \quad u_2 ) \quad (3)$$

Man kan "gange" matricer og vektorer sammen når de passer i dimensionerne. Lad os definere dette konkret for specialtilfældet af en matrix-vektor multiplikation. En matrix ganget på en vektor giver en ny vektor hvis antallet af elementer i vektoren passer med antallet af søjler i matricen. Dvs hvis vi ganger  $\mathbf{A}$  på  $\mathbf{v}$  får vi en ny vektor  $\mathbf{y}$ :

$$\mathbf{y} = \mathbf{A}\mathbf{v} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} A_{11}v_1 + A_{12}v_2 \\ A_{21}v_1 + A_{22}v_2 \end{pmatrix} \quad (4)$$

For at gøre det helt konkret betragt så efterregn følgende eksempel:

$$\mathbf{A} = \begin{pmatrix} 5 & 6 \\ 1 & 4 \end{pmatrix} \quad (5)$$

$$\mathbf{v} = \begin{pmatrix} 2 \\ 3 \end{pmatrix} \quad (6)$$

$$\mathbf{y} = \mathbf{A}\mathbf{v} = \begin{pmatrix} 5 & 6 \\ 1 & 4 \end{pmatrix} \begin{pmatrix} 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 5 * 2 + 6 * 3 \\ 1 * 2 + 4 * 3 \end{pmatrix} = \begin{pmatrix} 28 \\ 14 \end{pmatrix} \quad (7)$$

Med diagonal elementer af en matrice forstås elementer på diagonalen fra øverst til venstre til nederst til højre. Altså  $A_{11}$  og  $A_{22}$  ovenfor. Samlet udgør alle disse elementer diagonalen på en matrix. Med en diagonal matrix forstås en matrix der har eksakt nul på alle elementer bortset fra diagonal elementerne. (Se ligning 6.16).

Bemærk at argumenterne imellem Bernath 6.12 og 6.16 beror på ting som i først lærer i Lineære Transformationer på 2 år, og man kan tage let på det nu (efter lineære transformationer er det simpelt). Pointen er at man altid kan finde nogle retninger således at intertensoren bliver diagonal. Det skal vi så her gøre fra starten for de molekyler vi ser på, så vi behøver ikke denne generelle måde nu. Dvs vi vil vælge koordinater for hvilke vi har formen i 6.16.

En matrix transponering er når man "vender den om". Hvis vi kalder den transporede af  $\mathbf{A}$  for  $\mathbf{A}^T$  gælder at

$$\mathbf{A}^T = \begin{pmatrix} A_{11} & A_{21} \\ A_{12} & A_{22} \end{pmatrix} \quad (8)$$

Bemærk at  $A_{12}$  og  $A_{21}$  byttede plads. Altså  $A_{ij}$  og  $A_{ji}$  bytter plads generelt. Denne operation kan man også lave med vektorer dvs en rækkevektor bliver en søjlevektor og vice versa.

$$\mathbf{v}^T = ( v_1 \quad v_2 ) \quad (9)$$

$$\mathbf{u}^T = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \quad (10)$$

Bemærk at man kan lave et vektor dot-produkt på denne måde som en matrix\*vektor multiplikation i specialtilfældet hvor matricen i virkeligheden bare er en række-vektor. For eksempel er matrix produktet imellem  $\mathbf{u}$  og  $\mathbf{v}$  er helt veldefineret som givende en vektor med et element, og det er jo så bare et tal

$$\mathbf{u}\mathbf{v} = (u_1 * v_1 + u_2 * v_2) \quad (11)$$

Det kan man også gøre for transponerede vektorer. Altså for eksempel en vector transponeret multipliceret med sig selv

$$\mathbf{v}^T\mathbf{v} = ( v_1 \quad v_2 ) \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = (v_1 * v_1 + v_2 * v_2) \quad (12)$$

Man ser altså det faktisk er normkvadratet på vektoren.

Med taleksemplet ovenfor får

$$\mathbf{v}^T\mathbf{v} = ( 2 \quad 3 ) \begin{pmatrix} 2 \\ 3 \end{pmatrix} = 2 * 2 + 3 * 3 = 13 \quad (13)$$

Det definerer notationen i ligning 6.18.

## Chapter 6

# Rotational Spectroscopy

### 6.1 Rotation of Rigid Bodies

The classical mechanics of rotational motion of a rigid body remains a relatively mysterious subject compared to that for linear motion. In order to dispel some of the mystery it is useful to note the extensive correspondence between linear motion of a point particle of mass  $m$  and rotational motion of the same particle (Figure 6.1 and Table 6.1). For simplicity the vector natures of most of the quantities are suppressed. The correspondences between the analogous linear and angular quantities in Table 6.1 are quite striking. The linear and angular variables are related by various equations,

$$\begin{aligned} \theta &= \frac{x}{r} \\ \omega &\approx \frac{v}{r} & (\boldsymbol{\omega} \times \mathbf{r} = \mathbf{v}) \\ a &= \frac{v^2}{r} & (\text{constant } \omega) \\ \mathbf{L} &= r\mathbf{p} & (\mathbf{L} = \mathbf{r} \times \mathbf{p}) \\ T &= rF & (T = \mathbf{r} \times \mathbf{F}) \end{aligned}$$

in which the full vector forms are listed in parentheses. For a single particle, the angular velocity  $\boldsymbol{\omega}$  and the angular momentum  $\mathbf{L}$  are vectors that point out of the plane of the rotation. In this case, the  $\boldsymbol{\omega}$  and  $\mathbf{L}$  vectors point in the same direction (Figure 6.2). If an extended object is rotating, then  $\mathbf{L}$  and  $\boldsymbol{\omega}$  need not point in the same direction (Figure 6.3). This behavior is represented mathematically by the matrix product

$$\mathbf{L} = \mathbf{I}\boldsymbol{\omega}, \quad (6.1)$$

where  $\mathbf{I}$  is represented by a symmetric  $3 \times 3$  matrix with equation (6.1) written explicitly as

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}. \quad (6.2)$$

The matrix  $\mathbf{I}$  is called the *moment of inertia tensor* in classical mechanics.

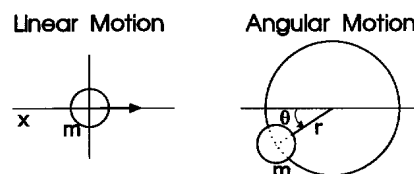


Figure 6.1: Linear and circular motion of a particle of mass  $m$ .

Table 6.1: The Correspondence between Linear and Angular Motion

Linear Motion	"Property"	Angular Motion
Distance, $x$	<i>Position</i>	Angle, $\theta$
Velocity, $v = \dot{x} = dx/dt$	<i>Velocity</i>	Angular velocity, $\omega = \dot{\theta} = d\theta/dt$
Acceleration, $a = \ddot{x} = d^2x/dt^2$	<i>Acceleration</i>	Angular acceleration, $\alpha = \dot{\omega} = d^2\theta/dt^2$
Mass, $m$	<i>Mass</i>	Moment of inertia, $I = mr^2$
Linear momentum, $p = mv$	<i>Momentum</i>	Angular momentum, $L = I\omega$
$E_k = \frac{1}{2}mv^2 = p^2/2m$	<i>Kinetic energy</i>	$E_k = \frac{1}{2}I\omega^2 = L^2/2I$
Force, $F$	<i>Force</i>	Torque, $T$
$F = ma = dp/dt$	<i>Newton's 2nd law</i>	$T = I\alpha = dL/dt$

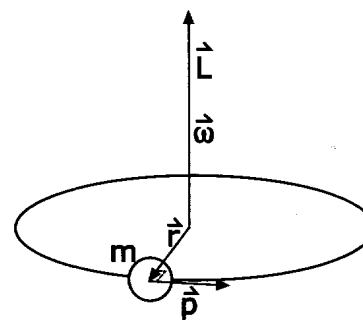
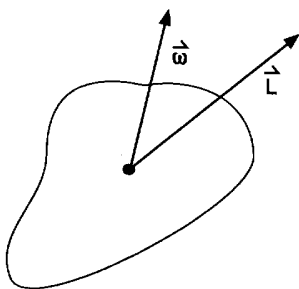
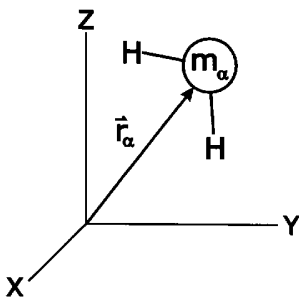


Figure 6.2: The circular motion of a particle of mass  $m$ .

The derivation of the form of the moment of inertia tensor for a collection of nuclei rotating together requires the use of some vector identities and the definition of angular momentum. Consider a collection of nuclei of mass  $m_\alpha$  located at positions  $\mathbf{r}_\alpha$  relative

Figure 6.3: For an extended object  $\omega$  and  $L$  can point in different directions.Figure 6.4: A typical molecule with nuclei located by  $r_\alpha$  vectors.

to the origin in a Cartesian coordinate system (Figure 6.4) and all rotating with angular velocity  $\omega$ , so that the angular momentum is given by

$$\mathbf{L} = \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{p}_{\alpha} = \sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha} \times (\boldsymbol{\omega} \times \mathbf{r}_{\alpha}), \quad (6.3)$$

in which

$$\boldsymbol{\omega}_{\alpha} = \boldsymbol{\omega} \quad \text{and} \quad \mathbf{p}_{\alpha} = m_{\alpha} \mathbf{v} = m_{\alpha} \boldsymbol{\omega} \times \mathbf{r}.$$

The cross product identity

$$\mathbf{P} \times (\mathbf{Q} \times \mathbf{R}) = \mathbf{Q}(\mathbf{P} \cdot \mathbf{R}) - \mathbf{R}(\mathbf{P} \cdot \mathbf{Q}) \quad (6.4)$$

gives

$$\begin{aligned} \mathbf{L} &= \sum_{\alpha} m_{\alpha} (\boldsymbol{\omega}(\mathbf{r}_{\alpha} \cdot \mathbf{r}_{\alpha}) - \mathbf{r}_{\alpha}(\mathbf{r}_{\alpha} \cdot \boldsymbol{\omega})) \\ &= \sum_{\alpha} m_{\alpha} (\boldsymbol{\omega}(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - \mathbf{r}_{\alpha}(x_{\alpha}\omega_x + y_{\alpha}\omega_y + z_{\alpha}\omega_z)). \end{aligned} \quad (6.5)$$

Writing out the vector components gives

$$\begin{aligned} L_x &= \sum_{\alpha} m_{\alpha} (\omega_x(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - x_{\alpha}(x_{\alpha}\omega_x + y_{\alpha}\omega_y + z_{\alpha}\omega_z)) \\ &= \sum_{\alpha} m_{\alpha} (\omega_x(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - x_{\alpha}^2\omega_x - x_{\alpha}y_{\alpha}\omega_y - x_{\alpha}z_{\alpha}\omega_z) \\ &= \sum_{\alpha} m_{\alpha} (\omega_x(y_{\alpha}^2 + z_{\alpha}^2) - x_{\alpha}y_{\alpha}\omega_y - x_{\alpha}z_{\alpha}\omega_z) \\ L_y &= \sum_{\alpha} m_{\alpha} (\omega_y(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - y_{\alpha}(x_{\alpha}\omega_x + y_{\alpha}\omega_y + z_{\alpha}\omega_z)) \\ &= \sum_{\alpha} m_{\alpha} (\omega_y(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - y_{\alpha}^2\omega_y - x_{\alpha}y_{\alpha}\omega_x - y_{\alpha}z_{\alpha}\omega_z) \\ &= \sum_{\alpha} m_{\alpha} (\omega_y(x_{\alpha}^2 + z_{\alpha}^2) - x_{\alpha}y_{\alpha}\omega_x - y_{\alpha}z_{\alpha}\omega_z) \\ L_z &= \sum_{\alpha} m_{\alpha} (\omega_z(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - z_{\alpha}(x_{\alpha}\omega_x + y_{\alpha}\omega_y + z_{\alpha}\omega_z)) \\ &= \sum_{\alpha} m_{\alpha} (\omega_z(x_{\alpha}^2 + y_{\alpha}^2 + z_{\alpha}^2) - z_{\alpha}^2\omega_z - x_{\alpha}z_{\alpha}\omega_x - y_{\alpha}z_{\alpha}\omega_y) \end{aligned} \quad (6.6)$$

which can also be expressed in matrix form as

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} \sum_{\alpha} m_{\alpha}(y_{\alpha}^2 + z_{\alpha}^2) & -\sum_{\alpha} m_{\alpha}x_{\alpha}y_{\alpha} & -\sum_{\alpha} m_{\alpha}x_{\alpha}z_{\alpha} \\ -\sum_{\alpha} m_{\alpha}y_{\alpha}x_{\alpha} & \sum_{\alpha} m_{\alpha}(x_{\alpha}^2 + z_{\alpha}^2) & -\sum_{\alpha} m_{\alpha}y_{\alpha}z_{\alpha} \\ -\sum_{\alpha} m_{\alpha}z_{\alpha}x_{\alpha} & -\sum_{\alpha} m_{\alpha}z_{\alpha}y_{\alpha} & \sum_{\alpha} m_{\alpha}(x_{\alpha}^2 + y_{\alpha}^2) \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}. \quad (6.7)$$

Let us now identify the diagonal matrix elements of the matrix  $\mathbf{I}$  as

$$I_{xx} = \sum_{\alpha} m_{\alpha}(y_{\alpha}^2 + z_{\alpha}^2) = \sum_{\alpha} m_{\alpha}r_{\alpha,\perp}^2, \quad (6.8a)$$

$$I_{yy} = \sum_{\alpha} m_{\alpha}(x_{\alpha}^2 + z_{\alpha}^2) = \sum_{\alpha} m_{\alpha}r_{\alpha,\perp}^2, \quad (6.8b)$$

$$I_{zz} = \sum_{\alpha} m_{\alpha}(x_{\alpha}^2 + y_{\alpha}^2) = \sum_{\alpha} m_{\alpha}r_{\alpha,\perp}^2. \quad (6.8c)$$

These elements are referred to as the *moments of inertia*. Similarly, let us identify the nondiagonal matrix elements as

$$I_{xy} = -\sum_{\alpha} m_{\alpha}x_{\alpha}y_{\alpha}, \quad (6.9a)$$

$$I_{xz} = -\sum_{\alpha} m_{\alpha}x_{\alpha}z_{\alpha}, \quad (6.9b)$$

$$I_{yz} = -\sum_{\alpha} m_{\alpha}y_{\alpha}z_{\alpha}. \quad (6.9c)$$

These elements are referred to as *products of inertia*. Notice that the moment of inertia with respect to an axis involves the squares of the perpendicular distances of the masses from that axis, for example,  $r_{\alpha,\perp}^2$  from the  $x$ -axis.

In classical mechanics the motion of a collection of objects can be broken into the center of mass translational motion (see below) and the rotational motion about the center of mass. If a rigid rotor is assumed, the  $3N - 6$  internal vibrations are ignored.

The natural origin for the molecular coordinate system is the center of mass of the molecule.

The location of the center of mass (given by a vector  $\mathbf{R}$ ) for a system of total mass

$$M = \sum_{\alpha} m_{\alpha} \quad (6.10)$$

made up of a collection of particles is given by

$$M\mathbf{R} = \sum_{\alpha} m_{\alpha}\mathbf{r}_{\alpha}. \quad (6.11)$$

If the origin of the coordinate system is at the center of mass, then  $\mathbf{R} = 0$  and

$$\sum_{\alpha} m_{\alpha}\mathbf{r}_{\alpha} = 0. \quad (6.12)$$

The moment of inertia tensor is a real symmetric matrix, so it is always possible to find an orthogonal transformation matrix  $\mathbf{X}$  that transforms the moment of inertia tensor  $\mathbf{I}$  (in equation (6.7)) into diagonal form. The matrix  $\mathbf{X}$  represents a rotation of the coordinate system, which can be written as

$$\mathbf{r}' = \mathbf{X}^{-1}\mathbf{r} \quad \text{or} \quad \mathbf{r} = \mathbf{X}\mathbf{r}'. \quad (6.13)$$

The columns of the matrix  $\mathbf{X}$  are made up of the normalized eigenvectors of  $\mathbf{I}$ .

As discussed in Chapter 3, the diagonalized matrix  $\mathbf{I}'$  is related to the original matrix  $\mathbf{I}$  by a similarity transformation—that is,

$$\mathbf{I}\mathbf{X} = \mathbf{X}\mathbf{I}' \quad (6.14)$$

or

$$\mathbf{X}^{-1}\mathbf{I}\mathbf{X} = \mathbf{I}'. \quad (6.15)$$

The  $\mathbf{I}'$  matrix is a diagonal matrix whose elements are the eigenvalues of  $\mathbf{I}$ . This new coordinate system is called the *principal axis system* and  $\mathbf{I}'$  has the form

$$\mathbf{I}' = \begin{pmatrix} I_{x'x'} & 0 & 0 \\ 0 & I_{y'y'} & 0 \\ 0 & 0 & I_{z'z'} \end{pmatrix}. \quad (6.16)$$

In most work the use of the principal axis system is assumed so that the primes will be dropped and  $I_x = I_{x'x'}$ ,  $I_y = I_{y'y'}$ , and  $I_z = I_{z'z'}$ . In the principal axis system we write

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_x & 0 & 0 \\ 0 & I_y & 0 \\ 0 & 0 & I_z \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} \quad (6.17)$$

or  $L_x = I_x\omega_x$ ,  $L_y = I_y\omega_y$ , and  $L_z = I_z\omega_z$ . The kinetic energy expression also has the very simple form

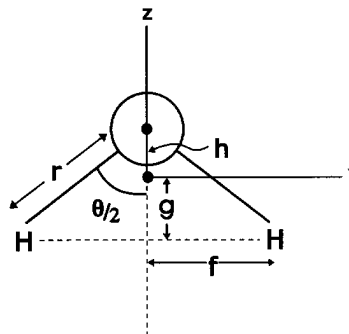


Figure 6.5: The  $\text{H}_2\text{O}$  molecule.

$$\begin{aligned} E_k &= T = \frac{1}{2}\boldsymbol{\omega}^t\mathbf{I}\boldsymbol{\omega} \\ &= \frac{1}{2}(\omega_x \ \omega_y \ \omega_z) \begin{pmatrix} I_x\omega_x \\ I_y\omega_y \\ I_z\omega_z \end{pmatrix} \\ &= \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 \\ &= \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}. \end{aligned} \quad (6.18)$$

The  $x$ -,  $y$ -, and  $z$ -axes are chosen by some set of geometrical conventions. For example, the  $z$ -axis of a molecule is always chosen to be the highest order axis of rotational symmetry, and the  $x$ -axis is out of the plane for a planar molecule. For example, the moments of inertia for the  $\text{H}_2\text{O}$  molecule (Figure 6.5) are

$$I_z = 2m_H f^2, \quad (6.19)$$

$$I_y = m_O h^2 + 2m_H g^2, \quad (6.20)$$

and

$$I_x = I_z + I_y = m_O h^2 + 2m_H(g^2 + f^2). \quad (6.21)$$

For any planar molecule the out-of-plane moment of inertia is equal to the sum of the two in-plane moments of inertia. There is another labeling scheme for the axes in a molecule based upon the magnitude of the moments of inertia. In this case, the axes are labeled  $a$ ,  $b$ , and  $c$  with

$$I_A \leq I_B \leq I_C \quad (6.22)$$

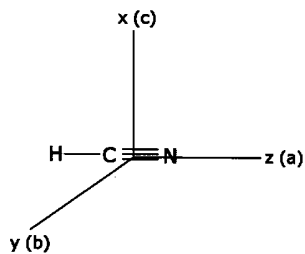


Figure 6.6: Linear molecule.

so that  $I_C$  is always the largest moment of inertia and  $I_A$  is the smallest. The  $a$ -,  $b$ -, and  $c$ -axes are chosen in order to ensure that this inequality holds.

For example, using  $r = 0.958 \text{ \AA}$ ,  $\theta = 104.5^\circ$ ,  $m_H = 1.00$  atomic mass unit (u), and  $m_O = 16.00$  u for  $\text{H}_2\text{O}$  results in  $f = 0.7575 \text{ \AA}$ ,  $g = 0.5213 \text{ \AA}$ , and  $h = 0.0652 \text{ \AA}$  using the center of mass definition (6.12). Thus from equations (6.19), (6.20), and (6.21) we obtain

$$I_z = 1.148 \text{ u \AA}^2 (= I_B)$$

$$I_y = 0.6115 \text{ u \AA}^2 (= I_A)$$

$$I_x = 1.760 \text{ u \AA}^2 (= I_C)$$

and  $z = b$ ,  $y = a$ , and  $x = c$ . There are six possible ways that  $(x, y, z)$  can be mapped into  $(a, b, c)$  depending on the particular values of the moments of inertia. The  $x$ -,  $y$ -,  $z$ -axes are picked by a customary set of rules, such as  $z$  is along the highest axis of rotational symmetry, but  $a$ ,  $b$ , and  $c$  are chosen to make equation (6.22) true.

Molecules can be classified on the basis of the values of the three moments of inertia. The five cases are as follows:

1. Linear molecules,  $I_B = I_C, I_A = 0$ ; for example, HCN (Figure 6.6).
2. Spherical tops,  $I_A = I_B = I_C$ ; for example,  $\text{SF}_6$  and  $\text{CH}_4$  (Figure 6.7).
3. Prolate symmetric tops,  $I_A < I_B = I_C$ ; for example,  $\text{CH}_3\text{Cl}$  (Figure 6.8).
4. Oblate symmetric tops,  $I_A = I_B < I_C$ ; for example,  $\text{BF}_3$  (Figure 6.9).
5. Asymmetric tops,  $I_A < I_B < I_C$ ; for example,  $\text{H}_2\text{O}$  (Figure 6.10).

Group theory can be used to classify the rotational properties of molecules. The spherical tops ( $O_h, T_d$ , and  $I_h$  point groups) and linear molecules ( $C_{\infty v}$  and  $D_{\infty h}$ ) are readily recognized. All symmetric tops have a  $C_n$ -axis, with  $n$  greater than 2. For example, the symmetric tops  $\text{CH}_3\text{Cl}$  and benzene have  $C_3$ - and  $C_6$ -axes, while the asymmetric top  $\text{H}_2\text{O}$  has only a  $C_2$ -axis. But what about allene (Figure 6.11)? By symmetry allene has  $I_B = I_C$ , and hence it must be a prolate symmetric top. Allene

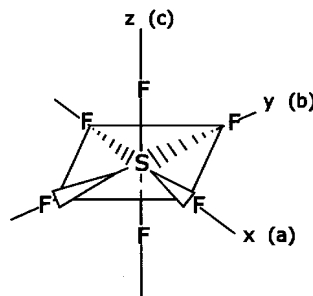


Figure 6.7: Spherical top.

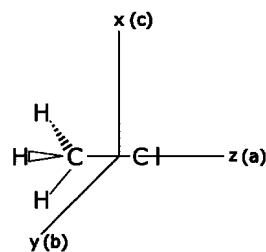


Figure 6.8: Prolate symmetric top.

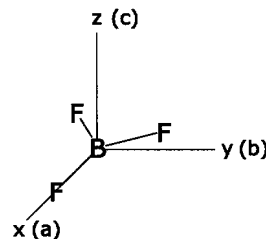


Figure 6.9: Oblate symmetric top.

has only a  $C_2$ -axis, but it does have an  $S_4$ -axis. The complete rule is, therefore, all molecules with a  $C_n$ -( $n > 2$ ) or an  $S_4$ -axis are symmetric tops. Note that the presence

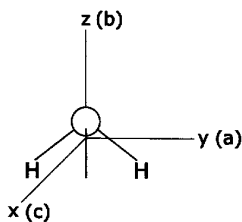


Figure 6.10: Asymmetric top.

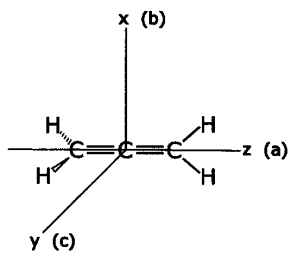


Figure 6.11: Allene, a symmetric top.

of an  $S_n$ -axis with  $n > 4$  implies the presence of a  $C_n$ -axis,  $n > 2$ , so this case need not be explicitly stated.

The symmetry properties of a molecule are also helpful in locating the principal axes. For example, if there is a  $C_n$ -axis with  $n > 1$ , then one of the principal axes lies along it (e.g.,  $H_2O$ ). Any molecule with a plane of symmetry has one of the principal inertial axes perpendicular to the plane (e.g.,  $H_2O$ ).

## 6.2 Diatomic and Linear Molecules

For a rigid linear molecule with no net orbital and spin angular momentum the classical expression for the rotational kinetic energy is, from equation (6.18),

$$\begin{aligned}
 E_k &= T = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 \\
 &= \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 \\
 &= \frac{J_x^2}{2I} + \frac{J_y^2}{2I} = \frac{J^2}{2I}
 \end{aligned} \tag{6.23}$$