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Solid angles 5. Chiral molecules and the case of face selectivity

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In this paper we present the analytical algorithm to calculate the solid angle of a collection of spheres in a hemisphere and quadrant. The methodology is a reliable and useful measure of partial steric congestion and can readily be applied to chiral and pro-chiral molecules. This algorithm lays the foundation for the application of a steric measure to the prediction of diastereomeric and enantiomeric excess.

1. Introduction

Theoretical models of chiral effects have been focused on two different areas: pure geometrical models of chiral objects [1] and molecular mechanics models of diastereoselectivity [2]. To our knowledge, there have been no mathematical models of chirality which can easily be applied to chemical systems [3]. Modeling of steric effects in chiral molecules poses an interesting challenge. By definition chiral isomers only differ in the spatial arrangement of their atoms so that conventional geometric measures of substituent size such as the cone [4] or solid angle [5] cannot be used to distinguish between enantiomers. From some common apex, both the linear and solid angles for each enantiomer will be identical. Prochiral molecules which contain non-equivalent faces are amenable to treatment by quantitative geometric steric measurements. Consider attack by a nucleophile at the carbonyl carbon of a chiral ketone. It is postulated [6] that the different stereoisomers arise because the path of the nucleophile is sterically hindered to a different degree on the *si*- and *re*-faces of the carbonyl. Conventional measures of steric size such as the Taft steric parameter [7] or cone angle [4] cannot easily be used to quantify this dif-

ference. However, the additivity of solid angles enables the theoretical treatment of such a problem.

The solid angle of an element of area, ds, subtended at a point, O, is

$$d\Omega = \frac{\boldsymbol{r}\cdot d\boldsymbol{s}}{r^3}\,, \tag{1}$$

where $\boldsymbol{r}$ is the vector from O to ds and r is its magnitude. It follows that the solid angle subtended by a surface, S, at O is

$$\Omega = \int_S \frac{\boldsymbol{r}\cdot d\boldsymbol{s}}{r^3}\,. \tag{2}$$

The integrand takes into account the three relevant factors: the size of the element of surface, its inclination to the line joining the element to O and the distance from O [8]. In terms of spherical polar co-ordinates, (2) becomes

$$\Omega = \int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1(\phi)}^{\theta_2(\phi)} \sin\theta\, d\theta = \int_{\phi_1}^{\phi_2} [\cos(\theta_1(\phi)) - \cos(\theta_2(\phi))]\, d\phi \tag{3}$$

in the general case for which the limits of the polar angle, θ, are functions of the azimuthal angle, ϕ. Solid angles are measured in steradians (sr). The solid angle can be thought of as the surface area, in steradians, occupied by the projection of the solid body on the inside of a unit sphere. If the solid body covers the entire unit sphere, then the solid angle of the body is 4π sr. If the solid angle is taken to be that of a cone, the vertex angle (commonly called the linear or cone angle) of the cone can be calculated [9]. It is important to note that solid angles are additive whereas cone angles are not additive.

To model the difference in steric demand on either side of a chiral plane, we need to define a steric measure to quantify the amount of occupied space on either side of the plane. If the reaction is under steric control, the side of the substrate with least steric congestion (i.e. the greatest amount of available space) is the preferred side of attack. To calculate the amount of occupied space relative to each molecular face, a plane is placed through the molecule and the solid angle on either side of this plane is calculated. The aim of this paper is to present an algorithm for the calculation of solid angles on opposite sides of a plane.

2. Application of solid angles to chirality

Consider the example of nucleophilic attack on a carbonyl group as illustrated in fig. 1. The Newman projections show the two different attack paths for the nucleophile in fig. 2. It is thought that the amount of steric congestion on either side of the plane defined by the sp^2 carbon atom determines which face the nucleophile attacks preferentially [6]. However, the solid angles of the portions of the molecule on either side of the plane of the sp^2 carbon atom are identical. If a second

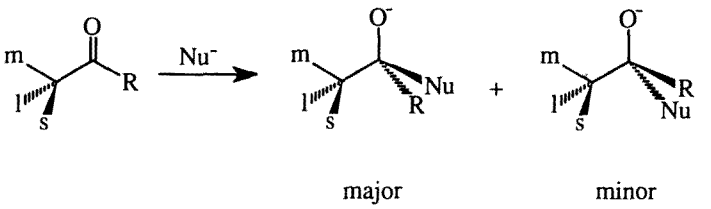

Fig. 1. Illustration of the nucleophilic attack on a carbonyl. The positions marked *s*, *m* and *l* refer to small, medium and large sized substituents, respectively. Note that the nucleophile can attack from either side of the chiral plane defined by the sp^2 carbon atom.

plane perpendicular to the first is added, then the solid angles of the portions of the molecule in the two quadrants (one for each diastereomer) in which attack occurs are different. Accepting the steric argument above [6], the amount of available space in the two quadrants of interest determines the rate of attack of the nucleophile at the carbon center. The rate of attack of the nucleophile, in turn, determines the diastereomeric excess of the products. The amount of space available can be deduced from the total solid angle in the required quadrant.

Let us first consider the simple system *AOB* (fig. 3), i.e. the case of two spheres, *A* and *B*, of different sizes (let $r_A < r_B$) placed at different distances from a common point, *O*, and suppose $OA > OB$. (These are for convenience of the diagram and have no specific implications for the discussion.) A plane is placed through the two spheres *A* and *B* so that it contains the common point *O* and does not coincide with an axis of symmetry (fig. 3). Since there is no symmetry about the plane (as shown in fig. 3), the total solid angles of the spheres from the perspective of *O* on either side of the plane will be different. When a solid angle of a molecule is calcu-

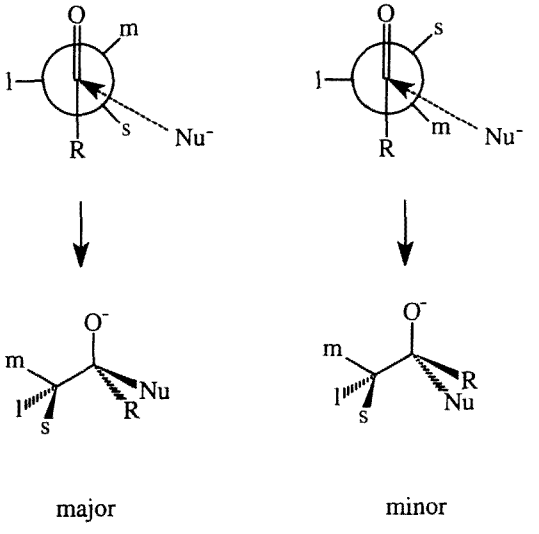

Fig. 2. Newman projections of two favored attack modes of the reaction illustrated in fig. 1.

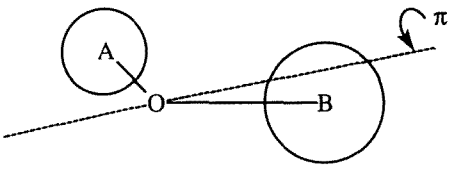

Fig. 3. Diagram of an arbitrary plane, π, passing through any part of a system where two spheres are attached to a common point.

lated, the molecule is projected onto the inside of a unit sphere and the maximum possible solid angle is 4π sr. When the solid angle on a single side of a plane is calculated, a portion of the molecule is projected onto the inside of a unit hemisphere and the maximum solid angle is 2π sr. Let χ be the solid angle of residual space (i.e. $\chi = 4\pi - \Omega$ or $2\pi - \Omega$; Ω = solid angle of the molecule or portion of molecule). The solid angle of residual space, χ, depends on the size of the sphere(s) in the hemisphere of interest. We now have a measure of both occupied (Ω) and unoccupied (χ) space in the molecule. Therefore we can differentiate between the two different hemispheres by means of Ω or χ. This approach is general for any geometrical arrangement of any number of spheres. Note that for the special case of $AOB = 180°$, with the plane placed in such a way as to contain the AOB plane, or any axis of symmetry, the space occupied on either side of the plane will be identical. This case need not be considered further since it provides no information about diastereofacial selectivity. In general the location of the plane is not important, but it should be generated in such a way that it does not contain any axis of symmetry of the molecule.

A second plane, perpendicular to the first one, can be defined (fig. 4). This divides the unit sphere into quadrants. The maximum solid angle in each quadrant is π sr and so a value of χ for the quadrant can also be determined. Once again the value of χ depends on the sizes and positions of the spheres in the quadrant. As with

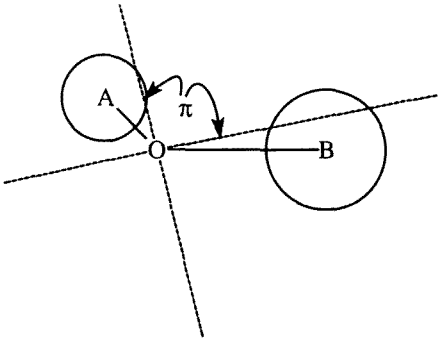

Fig. 4. Placement of a second plane, π, in a similar arrangement to the one illustrated in fig. 3.

the hemisphere approach this can also be generalized to any geometrical arrangement of any number of spheres.

The algorithm for calculating the total solid angle in a hemisphere or quadrant is presented below. Four cases are considered: (i) the plane cuts no atoms, (ii) the plane cuts a single sphere, (iii) the plane cuts two atoms which are not intersecting and (iv) the plane cuts two atoms which are intersecting. When the plane cuts no atom, the general solid angle algorithm [5] is applied to the atoms on the side of the plane of interest without modification. When the solid angle, Ω, is computed, the residual solid angle, χ, is given by $2\pi - \Omega$. As always in this paper the side of interest is that side of the plane for which the solid angle is sought just as the point of interest is that point (often termed the point of observation) from which the solid angle is measured.

3. Solid angles on one side of a plane

The original version of the general solid angle algorithm [5] needs to be modified in order to take into account a plane passing through the molecule and containing the point of interest. We assume that there is a plane through the molecule and there is interest in the steric effect of one side of the plane at a time. In the case of a single atom (sphere) we have the situation illustrated in fig. 5.

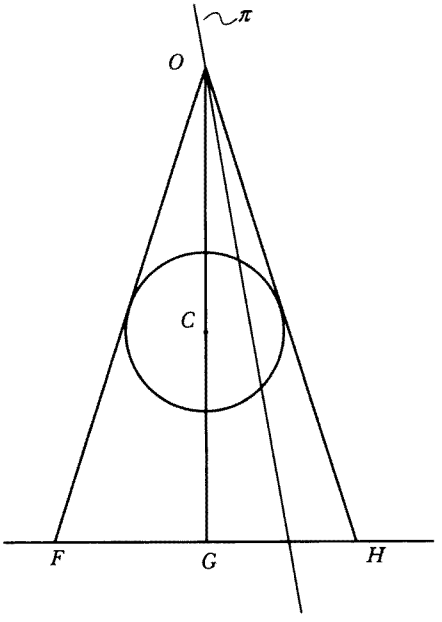

Fig. 5. A section of the system: sphere S and plane π by the plane perpendicular to π passing through the center C of the sphere S.

For the time being we select axes such that the x axis lies in the plane. The region of interest, i.e. for which Ω and χ are to be calculated, is taken to be above the plane (fig. 6).

The equation of the plane passing through the molecule and containing the point of observation, O, is

$$ox + my + nz = 0\,, \tag{4}$$

where

$$\hat{\boldsymbol{p}} = (o, m, n)^{\mathrm{T}} \tag{5}$$

is the normal to the plane in the direction of the area of interest. At a distance d below the xy plane where $z = -d$, since $x = 0$, the y ordinate in the plane is

$$y = nd/m\,. \tag{6}$$

The solid angle subtended by SMRN is

$$\begin{aligned}\Omega &= \int_S d\phi\, d\theta\, \sin\,\theta \\ &= \int_{HGR}^{HGS} [\cos\theta_{GM} - \cos\,\theta_{GN}]\, d\phi\,,\end{aligned} \tag{7}$$

where

$$\cos\theta_{GM} = \frac{OG}{OM} = \frac{OG}{(OG^2 + GM^2)^{1/2}} \tag{8}$$

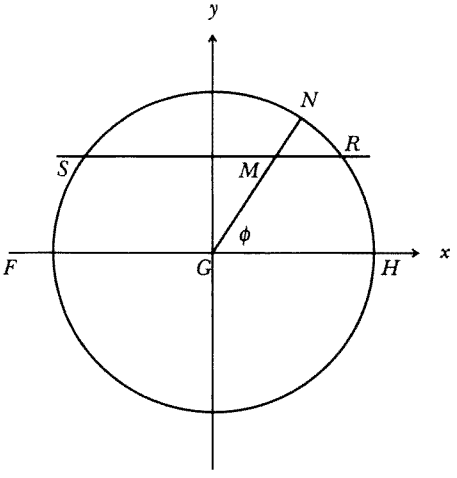

Fig. 6. Stereographic projection of the sphere and intersecting plane onto the plane normal to the axis OG at G.

and θ_{GN} is simply the semi-vertex angle, α, of the enveloping cone in fig. 5. Since $y = x\tan\phi$, at M,

$$\cos\theta_{GM} = \left[1 + \frac{GM^2}{OG^2}\right]^{-1/2}$$
$$= \left[1 + \frac{x^2 + y^2}{d^2}\right]^{-1/2}$$
$$= \frac{m\sin\phi}{[m^2\sin^2\phi + n^2]^{1/2}}\,. \tag{9}$$

Hence

$$\Omega = \int_{HGR}^{HGS}\left\{\frac{m\sin\phi}{(1 - m^2\cos^2\phi)^{1/2}} - \cos\alpha\right\}d\phi$$
$$= [\arccos(m\cos\phi) - \phi\cos\alpha]_{HGR}^{HGS}\,. \tag{10}$$

The values of the angles are given by the points of intersection of the line SR with the circle

$$x^2 + y^2 = d^2\tan^2\alpha\,, \tag{11}$$

which with $x\tan\phi = y$ and $y = (nd/m)$ gives

$$\cos^2\phi = \frac{m^2n^2\sin^2\alpha}{m^2} \tag{12}$$

so that

$$\Omega = \arccos\left[-(m^2 - n^2\sin^2\alpha)^{1/2}\right] - \arccos\left[(m^2 - n^2\sin^2\alpha)^{1/2}\right]$$
$$- \cos\alpha\left\{\arccos\left[-\frac{1}{|m|}(m^2 - n^2\sin^2\alpha)^{1/2}\right]\right\}$$
$$- \cos\alpha\left\{\arccos\left[\frac{1}{|m|}(m^2 - n^2\sin^2\alpha)^{1/2}\right]\right\}, \tag{13}$$

in which care must be taken in evaluating the inverse cosine to ensure that the correct branch is taken. This is determined by the sign of n/m.

When two atoms are to be considered, the choice must be made as to what determines the coordinate axes, the line between the centers of the two atoms or the orientation of the plane. We choose the former since all of the algebra has been done [5]. The plane is still taken to pass through the origin, but now has equation

$$lx + my + nz = 0\,, \tag{14}$$

where

$$\hat{\boldsymbol{p}} = (l, m, n)^{\mathrm{T}} \tag{15}$$

is in the direction of interest. The projected ellipses have equations

$$\text{(left)} \quad \frac{(x+c)^2}{a^2} + \frac{y^2}{b^2} = 1\,,$$

$$\text{(right)} \quad \frac{(x-c')^2}{a'^2} + \frac{y^2}{b'^2} = 1 \tag{17}$$

as shown previously [5]. The equation of the line is

$$lx + my = nd\,. \tag{18}$$

We assume that the line intersects both ellipses twice (figs. 7 and 8). For the sake of convenience we treat the cases in which the line passes above or below the origin separately and adopt the convention that the area of interest is above the line.

In fig. 7, T represents a typical point traversing the boundary of the region. In fig. 8 the points U and V represent the two typical points traversing the boundary of the region of interest.

Figure 7 case: The minimum value of θ is zero and so

$$\begin{aligned}\Omega &= \int_{-}^{-} d\phi \int_{0}^{\theta_B} \sin\theta \, d\theta \\ &= \int_{-}^{-} (1 - \cos\theta_{\mathrm{B}}) \, d\phi\,,\end{aligned} \tag{19}$$

where $\theta_{\mathrm{B}}(\phi)$ is the angle on the boundary. The limits for ϕ will be specified below. The boundary is traversed in three sections since $z = -d$. The first is from S to P on the right ellipse, the second is from P to N on the left ellipse and the third contained in the plane is from N to S along the straight line.

As usual

$$\cos\theta_{\mathrm{B}} = \frac{OG}{(OG^2 + GT^2)^{1/2}}\,. \tag{20}$$

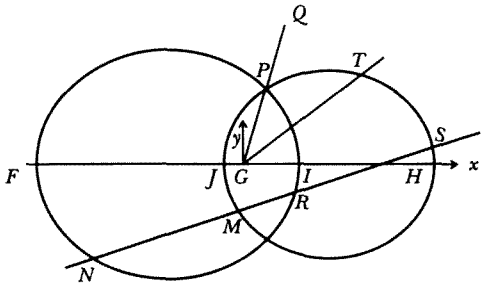

Fig. 7. Standard setup for two ellipses and a line passing below the origin in the plane, G.

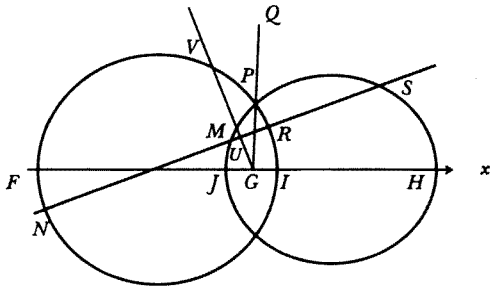

Fig. 8. Standard setup for two ellipses and a line passing above the origin in the plane, G.

Since $y = x\tan\phi$, eq. (20) gives

$$x = \frac{nd}{1 + m\tan\phi} \tag{21}$$

so that

$$GT^2 = \frac{n^2 d^2}{(l\cos\phi + m\sin\phi)^2} \tag{22}$$

and

$$\cos\theta_B = \frac{1}{\left[1 + \dfrac{n^2}{(l\cos\phi + m\sin\phi)^2}\right]^{1/2}}$$

$$= \frac{l\cos\phi + m\sin\phi}{[1 - (l\sin\phi - m\cos\phi)^2]^{1/2}}\,. \tag{23}$$

The integral can be evaluated as

$$\int \cos\theta_B \, d\phi = \arcsin(l\sin\phi - m\cos\phi)\,. \tag{24}$$

Hence (19) becomes

$$\Omega = 2\pi - \int_{HGS}^{HGP} (1 + \zeta_+^2)^{-1/2}\, d\phi - \int_{HGP}^{HGN} (1 + \eta_+^2)^{-1/2}\, d\phi$$
$$- \{\arcsin(l\sin HGS - m\cos HGS) - \arcsin(l\sin HGN - m\cos HGN)\}, \tag{25}$$

where η and ζ are

$$\eta_{\pm} = \frac{-\frac{c}{a^2}\cos\phi \pm \left[\frac{c^2}{a^4}\cos^2\phi + \left(1-\frac{c^2}{a^2}\right)\left(\frac{\cos^2\phi}{a^2}+\frac{\sin^2\phi}{b^2}\right)\right]^{1/2}}{\frac{\cos^2\phi}{a^2}+\frac{\sin^2\phi}{b^2}}, \tag{26}$$

$$\zeta_{\pm} = \frac{\frac{c'}{a'^2}\cos\phi \pm \left[\frac{c'^2}{a'^4}\cos^2\phi + \left(1-\frac{c'^2}{a'^2}\right)\left(\frac{\cos^2\phi}{a'^2}+\frac{\sin^2\phi}{b'^2}\right)\right]^{1/2}}{\frac{\cos^2\phi}{a'^2}+\frac{\sin^2\phi}{b'^2}} \tag{27}$$

as defined previously [5].

Figure 8 case: The minimum value of θ is now that given by the line and we denote it by θ_l and reserve θ_B for the curved parts of the boundary. The solid angle is given by

$$\Omega = \int_{-}^{-} (\cos\theta_l - \cos\theta_B)\, d\phi \tag{28}$$

and can be written down in terms of what has been defined above.

$$\Omega = \arcsin(l\sin HGN - m\cos HGN) - \arcsin(l\sin HGS - m\cos HGS)$$

$$- \int_{HGS}^{HGP} (1+\zeta_+^2)^{-1/2}\, d\phi - \int_{HGP}^{HGN} (1+\eta_+^2)^{-1/2}\, d\phi\,. \tag{29}$$

There are some variations to the results in (25) and (29). Consider the case of fig. 9 which is that of fig. 7 except that the positions of M and R are reversed.

Now there is a (small) region $P'MR$ which must be excluded. Evidently,

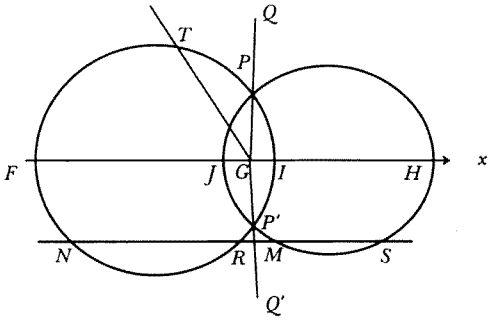

Fig. 9. The line $NRMS$ cuts both ellipses twice, but is not within the two ellipses over the line segment RM. NS does not have to be parallel to FH.

$$\Omega = 2\pi - \int_{HGS}^{HGP} (1+\zeta_+^2)^{-1/2}\, d\phi - \int_{HGP}^{HGN} (1+\eta_+^2)^{-1/2}\, d\phi$$
$$- \{\arcsin(l\sin HGR - m\cos HGR) - \arcsin(l\sin HGN - m\cos HGN)\}$$
$$- \int_{HGR}^{HGP'} (1+\eta_+^2)^{-1/2}\, d\phi - \int_{HGP'}^{HGM} (1+\zeta_+^2)^{-1/2}\, d\phi$$
$$- \{\arcsin(l\sin HGS - m\cos HGS)$$
$$- \arcsin(l\sin HGM - m\cos HGM)\}\,. \tag{30}$$

The case corresponding to fig. 8 is illustrated in fig. 10, the solid angle is given by

$$\Omega = \{\arcsin(l\sin HGM - m\cos HGM) - \arcsin(l\sin HGS - m\cos HGS)\}$$
$$+ \{\arcsin(l\sin HGN - m\cos HGN) - \arcsin(l\sin HGR - m\cos HGR)\}$$
$$- \int_{HGS}^{HGM} (1+\zeta_+^2)^{-1/2}\, d\phi \int_{HGR}^{HGN} (1+\eta_+^2)^{-1/2}\, d\phi\,. \tag{31}$$

4. Solid angles in a quadrant

We assume that the global coordinate system has been chosen so that the region of interest is specified by the planes $X = 0$ and $Y = 0$ (fig. 11). The equations of these planes are required in terms of the local coordinates (x, y, z) in which the point G is given by $(0, 0, -d)$. Since the plane normal to OG is not, in general, parallel to one of the coordinate planes in the (X, Y, Z) frame, the projections of the two planes, $X = 0$ and $Y = 0$, on this plane will not be at right angles.

The first task is to rotate the global axes to align them with the local axes at O. The point G is on the axis of the enveloping cone for the atom, or pair of atoms,

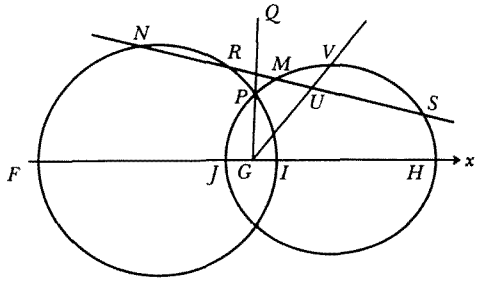

Fig. 10. The line NS cuts both ellipses twice, but it is not within the two ellipses over the line segment RM.

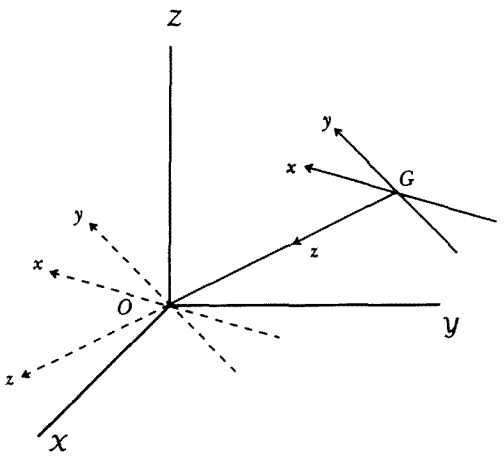

Fig. 11. Global and local coordinate frames.

under consideration and is located at a distance d from O as has been the case previously.

In global coordinates G is the point (X_G, Y_G, Z_G). Rotate about OZ so that the new coordinates $x'_G = 0$. In general,

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}' = \begin{pmatrix} \cos\mu & -\sin\mu & 0 \\ \sin\mu & \cos\mu & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \tag{32}$$

so that

$$x'_G = 0 = X_G \cos\mu - Y_G \sin\mu\,, \tag{33}$$

$$y'_G = 0 = X_G \sin\mu + Y_G \cos\mu\,, \tag{34}$$

$$z'_G = Z_G\,. \tag{35}$$

From (33) the angle μ is determined and then (34) gives the value of y'_G.

Now rotate about Ox' until $y''_G = 0$ and $z''_G = -d$.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}'' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\nu & -\sin\nu \\ 0 & \sin\nu & \cos\nu \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}' \tag{36}$$

so that

$$x''_G = 0\,, \tag{37}$$

$$y''_G = 0 = y'_G \cos\nu - z'_G \sin\nu\,, \tag{38}$$

$$z''_G = -d = y'_G \sin\nu + z'_G \cos\nu . \tag{39}$$

The combination of (35) and (36) gives ν in the correct quadrant.

This is sufficient if one is looking at a single atom (sphere). However, if one is considering a pair of atoms (spheres) it is necessary to make a further rotation, this time about z'' so that the new x axis is along the axis of symmetry of the two projected ellipses. We now have

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\lambda & -\sin\lambda & 0 \\ \sin\lambda & \cos\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} \tag{40}$$

and the overall transformation is

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\lambda & -\sin\lambda & 0 \\ \sin\lambda & \cos\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\nu & -\sin\nu \\ 0 & \sin\nu & \cos\nu \end{pmatrix} \begin{pmatrix} \cos\mu & -\sin\mu & 0 \\ \sin\mu & \cos\mu & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} . \tag{41}$$

When the two spheres are projected onto the base of a cone as in [5], the centers of the two spheres, C and D, lie on a line, FGH, which is to be the new x axis. Hence the y coordinates of (X_C, Y_C, Z_C) and (X_D, Y_D, Z_D) are to be zero. Both points are known from the molecular geometry and so there are two equations

$$0 = (X_C \cos\mu - Y_C \sin\nu)\sin\lambda + (X_C \sin\mu\cos\nu + Y_C \cos\mu\cos\nu - Z_C \sin\nu)\cos\lambda , \tag{42}$$

$$0 = (X_D \cos\mu - Y_D \sin\nu)\sin\lambda + (X_D \sin\mu\cos\nu + Y_D \cos\mu\cos\nu - Z_D \sin\nu)\cos\lambda , \tag{43}$$

which specify λ right down to the correct quadrant.

The inverse transformation is

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} \cos\mu & -\sin\mu & 0 \\ -\sin\mu & \cos\mu & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\nu & \sin\nu \\ 0 & -\sin\nu & \cos\nu \end{pmatrix} \begin{pmatrix} \cos\lambda & \sin\lambda & 0 \\ -\sin\lambda & \cos\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{44}$$

and this gives the relationship between the global coordinates and the local coordinates. The planes $X = 0$ and $Y = 0$ are described by the equations

$$x(\cos\mu\cos\lambda - \sin\mu\cos\nu\sin\lambda) + y(\cos\mu\sin\lambda - \sin\mu\cos\nu\cos\lambda) + z\sin\mu\sin\nu = 0 \tag{45}$$

and

$$-x(\sin\mu\cos\lambda+\sin\mu\cos\nu\sin\lambda)$$
$$+y(-\sin\mu\sin\lambda+\cos\mu\cos\nu\cos\lambda)+z\sin\mu\sin\nu=0\,, \tag{46}$$

respectively, and the two lines in the plane at G normal to OG are

$$lx+my=nd \tag{47}$$

and

$$l'x+m'y=n'd\,, \tag{48}$$

where the direction cosines (l, m, n) and (l', m', n') are given in terms of μ, ν and λ.

Note that $\langle(l, m, n), (l', m', n')\rangle = 0$ which is to be expected. However, $\langle(l, m), (l', m')\rangle \neq 0$ in general, i.e. the two lines in the plane are not mutually perpendicular.

In fig. 12 one possible set-up is illustrated. Note that the lines MN and PQ are generically not at right angles. It is assumed that both lines have been shown to intersect both ellipses twice. If this is not the case, the problem is one of the type discussed above. It is assumed that the region of interest is the right quadrant and the solid angle sought is that subtended by $SAHB$. Let GT be a ray from G which intersects the boundary of the region at U and V. If we denote the polar angle along MN as θ_{MN}, along PQ as θ_{PQ}, on the right ellipse as θ_R and on the left ellipse as θ_L,

$$\Omega=\int_{HGS}^{HGA}(\cos\theta_{PQ}-\cos\theta_{MN})\,d\phi+\int_{HGA}^{HGB}(\cos\theta_{PQ}-\cos\theta_R)\,d\phi\,, \tag{49}$$

where

$$\cos\theta_{MN}=\frac{l\cos\phi+m\sin\phi}{[1-(l'\sin\phi-m'\cos\phi)^2]^{1/2}} \tag{50}$$

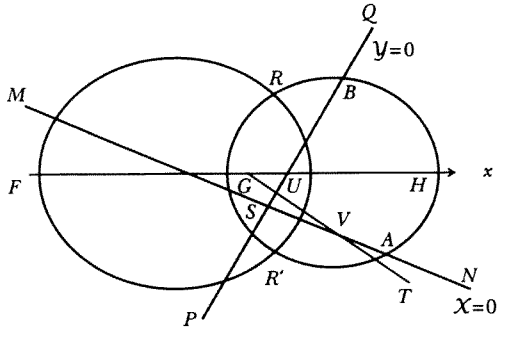

Fig. 12. The projections of $X = 0$ and $Y = 0$ onto the plane through G normal to OG.

$$\cos\theta_{PQ} = \frac{l'\cos\phi + m'\sin\phi}{[1 - (l'\sin\phi - m'\cos\phi)^2]^{1/2}} \tag{51}$$

(following (23)) and

$$\cos\theta_R = [1 + \zeta_+^2]^{-1/2} \tag{52}$$

(following from [5]).

Other possible line configurations are evident from the other three quadrants and the formulae can easily be written down.

5. Conclusion

The analytical algorithm for the calculation of the solid angle of a portion of a molecule in a hemisphere or a quadrant is presented. In our discussion we have not given every possibility as this would have added unnecessary length to the paper. We simply highlight the types of mathematical problems the computer code would have to address. We note that similar calculations could be made for octants, but they do not have immediate chemical application.

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