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Fundamentals of Chirality

And now, if e'er by chance I put
My fingers into glue
Or madly squeeze a right-hand foot
Into a left-hand shoe . . . .

Through the Looking-Glass, Lewis Carroll, 1871

Imagine a sophisticated three-dimensional scanner, capable of recording and encoding not only the precise shape of a physical object, but also the details of its texture, colouration, chemistry and mass distribution – in short, every aspect of its internal composition and outward appearance that one might perceive upon the most careful of inspections. Next, imagine that these encoded details are passed to a yet more sophisticated three-dimensional assembler, capable of reproducing a perfect physical replica of the original object, identical in every respect that can be observed or indeed measured. At the time of writing, such technology remains in the realm of science fiction, albeit recent advances in laser scanning and three-dimensional printing bring some superficial elements of the scheme within touching distance. Nevertheless, we can certainly conceive of the possibility of such a ‘replicator’, and consider its implications for our ability to distinguish between similar objects.

Now, if the replicator described above does its job perfectly, it is clear that the original object and its replica should be perfectly indistinguishable, once the former is removed from the scanner and the latter from the assembler. This much is inherent in our definition of the replicator, and should not unduly exercise our curiosity. A more interesting case may be found, however, when we make a subtle alteration to the replicator by swapping the sign of one spatial coordinate in the encoded details of the original object before passing it from the scanner to the assembler. The replica thus produced will then be identical to the original in every way except that it is its mirror image. Indeed, the replicator under these circumstances performs precisely the same transformation as a mirror, but unlike a mirror the ‘image’ it creates is substantial – capable of being picked up, moved, examined and dissected. Our question must now be whether the original and replica objects will still be indistinguishable, and our answer must, in general, be no.
The vast majority of natural objects placed into our doctored replicator will generate a replica that can be readily distinguished from the original. No amount of rotating or moving through space will succeed in making the original and the replica look precisely the same, and we shall recognise this fact by bestowing the adjective **chiral** to such objects. In fact, it is only in the case of objects possessing certain very particular symmetry properties that the original and replica will be indistinguishable – a situation that we shall recognise by describing such objects as **achiral**. The enumeration and categorisation of symmetry properties must therefore be our first concern.

### 1.1 Point and Space Groups

At the most fundamental level, symmetry refers to the property of an object whereby some **transformation** performed upon that object leaves it indistinguishable from its initial state. A plain cube, for example, may be rotated by 90° about a certain axis passing through its centre, and were it not for having observed the act in progress, it would otherwise be impossible to determine subsequently whether any action had been performed at all. This transformation may thus be said to be a **symmetry operation** of the cube, and the axis about which it occurs is said to be a **symmetry element** of the same. More specifically, this particular axis may be described as a fourfold axis, to indicate that four repetitions of the corresponding symmetry operation will return the system to its *literal* starting configuration, as opposed to a configuration that is simply indistinguishable from it.

To enumerate mathematically the various geometrical transformations that may turn out to be symmetry operations of a given object, it is convenient to employ vector notation. Let the three-dimensional vector \( \mathbf{p} \) represent some specific point within the object, and the three-dimensional vector \( \mathbf{p}' \) that same point after undergoing some transformation. The transformed vector is then related to the original vector by the equation

\[
\mathbf{p}' = R\mathbf{p} + T + t
\]

where \( R \) is a \( 3 \times 3 \) matrix, and both \( T \) and \( t \) are three-dimensional vectors. The matrix \( R \) can effect **rotation**, **reflection**, **inversion** or **scaling** (or combinations thereof) whilst the vectors \( T \) and \( t \) each effect spatial **translation**; the symbol \( T \) is reserved for translations corresponding to Bravais lattice vectors within a crystalline material, whereas \( t \) stands for any other non-Bravais translation. Applying the same geometrical transformation to all points within the object then achieves the corresponding geometrical transformation of the entire object. The act of scaling an object can never leave it apparently identical to its original state, so scaling transformations can never be symmetry operations of an object.\(^1\) Rotation, reflection and inversion operations *can* all be symmetry operations of certain objects, with associated symmetry elements consisting of

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\(^1\) Unless that object happens to be a perfect fractal, which physical objects never are.
rotation axes, mirror planes and centres of inversion, respectively, together
with so-called rotoreflection axes corresponding (unsurprisingly) to a
combination of rotation and reflection.

The special case of a null rotation (i.e. rotating through zero angular displace-
ment) combined with null translation (i.e. translating through zero linear dis-
placement) is described as the identity operation, and leaves the object entirely
unmoved. More general transformations for which the net translational vector
$\mathbf{T} + \mathbf{t}$ is null are known as point operations, because they leave at least one point
in space entirely unmoved, while those for which the net translational vector is
finite may be described as space operations. Clearly, the distinction between
the two categories can be highly dependent upon one’s choice of origin. Space op-
erations that can be reduced to point operations by a suitable choice of origin are
known as symmorphic operations. Space operations that cannot be reduced to
point operations by a suitable choice of origin are known as non-symmorphic
operations, of which the glide symmetry operation (a combination of reflection
across a plane with translation through half of a Bravais lattice vector lying within
that plane) and the screw symmetry operation (a combination of rotation about
an axis with translation by some fraction of a Bravais lattice vector lying along
that axis) are the commonly recognised examples.

The set of all possible symmetry operations for a given object is known as its
space group, and may in general contain both point and space operations. For a
spatially finite object (such as a molecule) all of these operations are necessarily
symmorphic, but for a spatially periodic object (such as a perfect crystal) both
symmorphic and non-symmorphic space operations may arise. A space group
containing only symmorphic operations is said to be a symmorphic space group,
while one that contains even a single non-symmorphic operation is said to be a
non-symmorphic space group.

The set of transformations obtained by simply omitting the translational com-
ponent from each symmetry operation of the space group of an object is known
as the point group of the space group. In the case of a spatially finite object, the
point group of the space group is identical to the space group for one particular
choice of origin. For a spatially periodic object, however, this will only be true if
the space group is symmorphic; otherwise, the point group of the space group
will contain transformations distinct from the symmetry operations of the space
group, whatever the choice of origin. In either case, the point group of the space
group consists of a set of exclusively point operations. Furthermore, in the case
of a spatially periodic object, it is this point group and not the space group that
will constrain the macroscopic shape (and all other macroscopic properties) of
that object.

It is worth noting very carefully that the point group of the space group of a
crystal is not necessarily synonymous with either ‘the set of all point symmetry
operations pertaining to the lattice’ or ‘the set of all point symmetry operations
pertaining to the crystal’. If the space group contains glide or screw operations,
then the point group of the space group will contain reflection or rotation sym-
metry operations that are not symmetries of the crystalline structure; conversely,
the point group of the space group may lack certain symmetry operations that
are indeed symmetry operations of the lattice. Despite the scope for ambiguity,
however, the point group of the space group is generally referred to as the point group of the crystal, and we shall follow this practice in all subsequent chapters.

1.2 Proper and Improper Symmetry

Amongst all the various symmetry operations that may be found within the point or space group of an object, those for which the matrix $R$ has a determinant equal to unity possess an important special property – they can actually be performed upon a rigid physical body in the real world, not just as a thought experiment or as a reflection in a mirror. Examples include, but are not limited to, the identity, rotation, translation and screw operations. Such operations are collectively described as proper symmetry operations.

In contrast, operations including, but again not limited to, the reflection, inversion and glide operations cannot be performed upon a rigid physical body in the real world. These are operations that can only be performed as a reflection in a mirror, or as a thought experiment, and they are collectively described as improper symmetry operations. The determinant of the matrix $R$ in these cases will be minus unity.

Sequential application of successive proper symmetry operations to an object achieves a resultant operation that is itself also a proper operation; the transformation matrix obtained by multiplying several matrices of unit determinant together will itself have a determinant of unity. Similarly, a sequence of operations in which an even number is improper will also result in a proper composite operation, since multiplying together their individual transformation matrices will again yield a matrix with unit determinant. Concatenating a sequence of operations for which the number of improper operations is odd, however, results in an improper combined operation, described by a transformation matrix whose determinant is minus unity.

The crucial significance of these definitions in our present considerations is that the mirror image of an object can be manipulated by a series of proper symmetry operations to look identical to the original object if, and only if, its space group contains at least one improper symmetry operation. Referring back to our earlier definition of chirality, this may be re-stated as:

An object whose space group contains no improper symmetry operations is necessarily chiral; the presence of even a single improper symmetry operation in the space group renders an object achiral.

This statement is precise and complete. It embodies the relatively obvious fact that an object possessing a mirror symmetry operation in its space group is achiral (since this implies straightforwardly that it is unchanged when reflected across a suitably oriented mirror plane) but also the somewhat less obvious fact that inversion or glide symmetries would be equally capable of ensuring that the object is achiral (even in the absence of mirror symmetry). Enumeration of the space group operations of an object, followed by their categorisation into
proper and improper types, provides a foolproof test for chirality and is to be favoured over attempts at visualising the effects of reflection and subsequent manipulation.

1.3 Chirality in Finitude and Infinity

As with all aspects of symmetry, the chirality of an object is intimately tied up with its dimensionality. Objects that may be achiral in zero-dimensional isolation may become chiral upon repetition within a two- or three-dimensional lattice, and vice versa. Since we shall be interested, ultimately, in chirality at surfaces, where zero-dimensional molecules meet three-dimensional solids, it makes sense to describe the chirality of those cases first, before tackling the two-dimensional realm of the surface itself.

1.3.1 Molecular Chirality

As we have mentioned already, the space group of a spatially finite object, such as a molecule, is practically synonymous with its point group. That is, for a particular choice of origin, only symmetry operations having no translational component need be considered. Permissible symmetry operations therefore comprise rotations, reflections and inversions alone (or their combinations). A point group containing only rotations (including the identity operation) lacks improper symmetry operations, and therefore indicates that the object is chiral; one that includes either reflections or inversions (or both) indicates an achiral object. Real molecules collectively exhibit a wide range of different point groups of both the chiral and the achiral varieties.

Consider, for example, the pyruvic acid molecule depicted in Fig. 1.1a. The point group of this molecule includes a reflection across a mirror plane (the plane containing the carbon and oxygen atoms) and therefore indicates that the molecule is achiral. In contrast, the lactic acid molecules depicted in Fig. 1.1b, which may be obtained from pyruvic acid by hydrogenation, each entirely lack reflection and inversion symmetry operations in their point groups, demonstrating that they are chiral. As a consequence of this chirality, lactic acid molecules

![Figure 1.1](image-url)
Chirality at Solid Surfaces

can be found in two forms, known as **enantiomers** (i.e. stereoisomers related to one another as mirror images). Enantiomers are necessarily energetically degenerate with one another and should arise in equal proportion in any process that is not in some sense asymmetric in nature.

Now, the symmetry properties of a molecule are clearly properties possessed by the molecule as a whole, not by some fragment of the molecule in isolation. It follows, therefore, that the chirality or otherwise of a molecule is also a property of the whole molecule, and we would do well to keep this important point always in mind. Nevertheless, it is clear in the case just described that chirality appeared when a particular kind of change was effected at one particular carbon atom, where hydrogenation occurs. In pyruvic acid, this carbon atom forms three bonds to different atoms or groups of atoms, and these bonds lie within the mirror plane of the molecule. In lactic acid, on the other hand, this carbon atom now forms four bonds to different atoms or groups of atoms, and these can no longer all lie within the same plane. This carbon atom is said to be a **chiral centre**, because it is the vital change in geometry at this site in lactic acid that breaks the improper symmetry found in pyruvic acid. In general, any atom (usually carbon) that forms bonds to four chemically or geometrically distinct atoms or groups of atoms will be a chiral centre; if fewer than four bonds are present, or if the bonded atoms or groups of atoms are not all distinct, then the central atom is not a chiral centre.

Molecules, such as pyruvic acid, featuring an atom that can be converted into a chiral centre in a single reaction step are designated **prochiral**, and are often of importance in synthetic pathways leading to chiral products.

One further advantage to identifying the chiral centre of a molecule arises in the matter of nomenclature. Clearly, the two enantiomers of lactic acid shown in Fig. 1.1b are distinct from one another, but normal chemical naming conventions are incapable of specifying which of the two we might be discussing at any given moment. The Cahn–Ingold–Prelog convention, however, provides an entirely robust procedure for assigning identifying labels to the enantiomers, as follows:

1) Identify the chiral centre of each enantiomer, assuming for the moment that there is only one;
2) Assign priorities to the groups surrounding the chiral centre, according to a more or less arcane set of rules based on the atomic numbers and connectivities of the constituent atoms;
3) Viewing the chiral centre from the direction precisely opposite to its lowest priority group, the label **R** is assigned if one sees a clockwise arrangement of the remaining groups from high to low priority, and the label **S** if the order is anticlockwise.

There is certainly some devilry in the detail of Step 2, which we shall not pursue further here; the interested reader is referred to the original description [1]. For our present purposes, it is sufficient merely to recognise that the labels **R** and **S** may be assigned unambiguously for any individual chiral centre. The letters **R** and **S**

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2 For this purpose, a well-defined lone pair may be considered as a dangling bond that counts to the same degree as a non-dangling bond.
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Figure 1.2 Chiral tartaric acid (R,R and S,S enantiomers) and the meso isomer (R,S-tartaric acid, equivalent to S,R-tartaric acid).

S stand, respectively, for the Latin words rectus and sinister – meaning ‘Right’ and ‘Left’ – but clearly the assignment is essentially arbitrary (albeit well defined) and does not correspond in any way to any essential quality of ‘rightness’ or ‘leftness’. Indeed, closely related molecules, differing only by a relatively minor substitution (e.g. replacement of an alcohol group by a thiol group) may acquire opposing R/S labels.

An alternative labelling convention, commonly applied when dealing with relatively simple chiral molecules, assigns labels D and L by making comparison with the enantiomers of glyceraldehyde. The R enantiomer of glyceraldehyde happens to effect a clockwise rotation in the plane of linearly polarised light (and is therefore said to be ‘dextrorotary’) whilst the S enantiomer causes an anticlockwise rotation (and is correspondingly said to be ‘laevorotary’). The prefixes dextro- and laevo- are, once again, of Latin origin and again refer to ‘right’ and ‘left’. Enantiomers (of other species) whose chiral centre may be synthesised through achiral chemistry from the dextrorotary form of glyceraldehyde are assigned the label D, while those that may be similarly synthesised from the laevorotary form are assigned the label L. Note that, once again, the procedure for assignment of labels is well defined (although more limited in applicability than the R/S convention) but apart from the case of glyceraldehyde itself, there is no link between the D/L labels and the property of dextro-/laevo-rotation.3

Although useful, the concept of a chiral centre must be invoked with care, as can be seen most clearly when a molecule contains two or more chiral centres. Consider the tartaric acid molecules depicted in Fig. 1.2, where each chiral centre has been labelled according to the Cahn–Ingold–Prelog convention. In the R,R and S,S cases, the point group of each molecule is devoid of reflection and inversion symmetries, and is thus chiral as we might have expected. In the R,S and S,R cases, however, each molecule possesses an inversion symmetry and is therefore achiral; in fact, these ‘two’ molecules are actually precisely the same molecule viewed from different perspectives. Tartaric acid can thus occur in a

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3 Indeed, it is important to distinguish the D and L labels described in the text, which do not imply the sense of optical rotation, from the labels d and l which explicitly do indicate the dextrorotary and laevorotary forms. In view of the potential for confusion, the usage of d/l to indicate rotary sense is now deprecated, and ± labels used instead to represent the same quality. It should go without saying that the R/S labels of the Cahn–Ingold–Prelog notation are no more indicative of rotary sense than are the D/L labels.
chiral form, with two enantiomers labelled $RR$ and $SS$, or in an achiral form in which the two chiral centres effectively cancel each other out. An achiral molecule in which two chiral centres negate one another is known as a **meso isomer**, and can only occur when the two chiral centres exist in otherwise identical parts of the molecule. More generally, of course, a molecule may have two chiral centres that exist in distinct parts of the molecule, in which case the $RR$ and $SS$ forms comprise one pair of enantiomers, while the $RS$ and $SR$ forms comprise a second pair of enantiomers not degenerate with the first.

Finally, it is very important to understand that a molecule may be chiral *without* possessing any chiral centres at all. A classic example may be found in the helicene molecules, where contiguous aromatic rings are connected so as to form a helical structure. No single atom can be identified as a chiral centre, yet these molecules are plainly chiral (see Fig. 1.3).

### 1.3.2 Crystalline Chirality

Turning to extended solid materials, it is customary to begin by ignoring the existence of any surfaces; in effect, one considers such a material to be infinite in extent. In the case of an amorphous solid, it is clear from the outset that all improper symmetry elements must be lacking, and hence that the object is chiral. This is, however, an essentially trivial form of chirality, since the exact mirror-image form of an amorphous solid is just one amongst an infinity of virtually degenerate alternative arrangements of the constituent atoms, rather than a practically realisable configuration. Non-trivial chirality in solids can only be spoken of when there is long-range order, so that a lack of improper symmetry really does imply the existence of enantiomeric configurations that can realistically be obtained and studied.

Let us, therefore, consider the range of possible space groups available to three-dimensional crystals. It turns out that there are precisely 230 of these, but the majority include improper symmetry operations and hence lead to crystals that are non-chiral. Only 65 of the space groups lack all improper symmetry...
operations, and crystals conforming to one of these so-called **Sohncke** space groups will necessarily be chiral.\(^4\)

Examples of chiral solids include cases, such as crystalline tartaric acid, where a chiral molecule forms the basis of the unit cell. Here, the chirality of the situation is demanded by the molecule, and the long-range ordering may or may not reflect the chirality (i.e. chiral molecules may be distributed through space within a non-chiral lattice). On the other hand, one also finds crystals, such as quartz, where there are no identifiably chiral sub-units, and in these cases it is precisely the long-range ordering that is responsible for chirality.

### 1.4 Routes to Surface Chirality

In considering surface chirality, it is worth dismissing (as above) those trivial cases where chirality is formally present due to the absence of improper symmetry, but practically absent because one is dealing with an amorphous or otherwise disordered system. We shall restrict ourselves, therefore, to the surfaces of crystalline materials, and to adsorption that leads to at least partial (if not complete) ordering of adsorbates. Even within these restrictions, there are several ways in which chirality may arise.

#### 1.4.1 Surfaces of Intrinsically Chiral Crystals

Perhaps the most obvious way in which surface chirality may arise occurs at the surfaces of chiral crystals. Clearly, if the underlying bulk material is itself already chiral, the creation of a surface (whether by cleavage, cutting or growth) cannot possibly add any of those improper symmetry elements whose presence would be needed to render the surface achiral. In this way, the surfaces of crystals such as quartz or tartaric acid, mentioned in the previous section, would necessarily be chiral, whatever orientation the surface takes. In terms of possible applications for chiral surfaces, one feature here is that the particular enantiomer to be used may be chosen at the level of the bulk material. Less conveniently, however, one is limited to only those materials that happen to crystallise in these forms; to date, the surface of quartz has dominated work in this area [2]. If one’s interest lies in asymmetric heterogeneous catalysis, for example, then the absence of chiral crystalline polymorphs for reactive transition metals would be problematic. It may, of course, be possible to use chiral crystals as support materials, in the hope that they may template the formation of reactive metals into asymmetric thin-films or nanoparticles, but this avenue has yet to be explored in depth.

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\(^4\) Confusingly, the term *chiral space group* is reserved *not* for the full set of 65 Sohncke space groups, but only for a subset of 22 space groups whose symmetry elements are not preserved upon applying an improper symmetry operation *to the space group*. It is self-evident that a space group whose formal structure is itself chiral can only give rise to a chiral crystal; the same is true, however, for the other 43 Sohncke space groups, whose symmetry elements are related to one another in an achiral fashion, but which simply do not include any that correspond to improper operations.
1.4.2 Intrinsically Chiral Surfaces of Achiral Crystals

Whenever the three-dimensional structure of a bulk crystal is terminated by a surface plane, there exists the possibility that certain of the symmetry operations of the bulk may be removed. The most trivial example would be where the surface plane lies parallel to a bulk mirror plane, in which case the mirror plane most certainly would not remain as a symmetry operation of the truncated material. More generally, all types of symmetry operation are potentially susceptible to being broken by the existence of the surface — which ones actually are broken in any given case will be determined by the space group of the bulk crystal and the particular orientation of the surface. Assuming the bulk crystal to be achiral, the possibility of surface chirality will be realised whenever the surface orientation is such as to remove all of the improper symmetry elements present in the bulk. In contrast to the examples in the preceding subsection, this form of surface chirality may be achieved, at least in principle, for any crystalline material, including those taking the highly symmetric face-centred cubic, body-centred cubic and hexagonal close-packed structures favoured by (chemically interesting) transition and coinage metals. Another advantage is that the same parent bulk material may be used to create surfaces of opposing chirality, simply by changing the orientation at which the surface is cut. The link between orientation and chirality will be thoroughly discussed in the next chapter, but for the moment we merely present a couple of examples to illustrate our point.

The fact that surfaces of achiral materials may be chiral by virtue of their intrinsic structure seems to have been explicitly discussed first by Gellman and co-workers [3] in a 1996 paper concerning the \{643\} surfaces of silver. They noted that surfaces possessing regularly kinked step-edges must be chiral if the length of step either side of each kink differs (see Fig. 1.4a). Furthermore, they introduced the idea of labelling the chirality of such surfaces within a convention inspired by the Cahn–Ingold–Prelog rules; the priority of groups surrounding a chiral centre was replaced with that of steps and terraces surrounding each chiral kink, arbitrarily defined in the (descending) order long-step/short-step/terrace. A little later, Ahmadi et al. [4] pointed out that the kinked surfaces of face-centred cubic materials would be chiral even if the step lengths were equal (e.g. in the \{531\} surface type, see Fig. 1.4b) and Attard subsequently proposed a modified version of the Cahn–Ingold–Prelog convention that has become the most widely used in the field [5]. This revised scheme is rooted in the observation that each kink site is necessarily surrounded by microfacets of \{111\}, \{100\} and \{110\} type, arbitrarily assigned (descending) priority in that order; if the microfacets cycle clockwise around the kink atom, in descending order of priority, the surface is labelled R, and conversely the designation S correlates with the anticlockwise sense. Although unambiguous, and relatively easy to use, this convention is limited when applied to materials of other crystalline structures. For example, some surfaces of body-centred cubic materials (e.g. the \{321\} surface type, see Fig. 1.4c) may be chiral despite the complete absence of kink sites. For this reason, an alternative notation has been proposed [6], in which the labels D and L are used, based upon the symmetry of crystallographic directions, rather than
the structure of microfacets; for face-centred cubic materials, the D and R labels correspond with one another, as do the L and S labels, but the approach is more widely applicable to other crystal structures, as we shall see in the next chapter.

1.4.3 Chiral Modification of Achiral Surfaces

Finally, we note the possibility that a surface whose structure is achiral when clean may be rendered chiral by the adsorption of chiral molecules. If these molecules arrange themselves in disordered fashion on the surface, then the long-range chirality thus obtained will be of a trivial nature, but one may still speak of non-trivial chirality at short length-scales (of the order of the molecular size); we might term this irreducible molecular chirality (as distinct from the contingent molecular chirality that may be induced in adsorbed achiral molecules). In such cases, the surface may now react in an asymmetric manner towards further chiral stimuli – surface chemical reactions, for instance, may
become enantioselective \(^5\) – but the mechanism must be explicable at a purely local level. On the other hand, it may be that adsorbed chiral molecules arrange themselves on the surface in a highly ordered fashion, and if they do so then it is further possible (though by no means certain) that they may adopt chiral long-range order; we might term this intrinsic lattice chirality if it is dictated by the overlayer lattice per se and extrinsic lattice chirality if it arises from the orientation of an otherwise achiral overlayer lattice relative to the underlying substrate lattice. If either of these situations arises globally, the surface ought once again to display an asymmetric response to chiral stimuli, but the origin of the asymmetry may lie in either the irreducible molecular chirality or the intrinsic/extrinsic lattice chirality (or some combination of both). Upon adsorption of an even-handed mixture of chiral molecules, domains of opposing local lattice chirality may occur, but the global behaviour will fail to display asymmetry, owing to degeneracy – mirror-image domains will arise in essentially equal proportion. On the other hand, even the adsorption of achiral molecules may result in locally lattice-chiral domains, once again displaying degeneracy and hence a lack of global asymmetry.

Furthermore, we ought also to recognise the possibility that adsorption of chiral molecules may induce a chiral reconstruction in the underlying substrate. Such a reconstruction might be ordered at long range (i.e. associated with a chiral lattice) or only at short range (e.g. the surface might break up into a series of facets, each locally ordered at the nanoscale but of varying size and shape at the mesoscale). In the case of a faceted surface, it may occur that some facet orientations are found to correspond to intrinsically chiral surfaces, in which case they may be said to display planar substrate chirality within themselves; nevertheless, even achiral facets may meet along low-symmetry edges or at low-symmetry vertices, in which case these may be viewed as loci of linear or pointlike substrate chirality.

The range of possible behaviours for adsorbed chiral molecules will be discussed in depth across several later chapters, but for the moment we simply emphasise the key distinctions between the length-scales and dimensionality pertaining to different forms of surface chirality. We summarise these as follows:

**Irreducible Molecular Chirality**

Chirality associated with a single molecule, and which cannot be removed without breaking at least one covalent bond. Such chirality in an adsorbate would typically be present even if the molecules were abstracted from the surface (e.g. alaninate is chiral not only when adsorbed on a surface, but also in solution).

**Contingent Molecular Chirality**

Chirality associated with a single molecule, but which can be removed without breaking even a single covalent bond. Such chirality in an adsorbate is typically related to internal deformation that would vanish if the molecules were abstracted from the surface (e.g. glycinate may adopt a chiral conformation when adsorbed on a surface, but is achiral in solution).

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\(^5\) We define an enantioselective reaction as one which proceeds with different rates for the two different enantiomers of the same chiral species.
**Figure 1.5** Intrinsic and extrinsic lattice chirality. In panel (a) the overlayer lattice, indicated with bold lines, is oblique in nature and would exhibit two mirror-image forms regardless of its relationship with the underlying substrate lattice, shown in feint lines. In panel (b) the overlayer lattice is square in nature, and would be achiral in isolation; chirality here derives only from the overlayer lattice’s misalignment with the substrate lattice.

**Intrinsic Lattice Chirality**
Chirality associated with the intrinsic nature of the two-dimensional lattice adopted by adsorbates. Such chirality (see Fig. 1.5a) is only present when the overlayer lattice is of oblique type (i.e. not of square, triangular, rectangular or rhombic symmetry).

**Extrinsic Lattice Chirality**
Chirality associated with the registry between the two-dimensional lattice adopted by adsorbates and that of the underlying substrate. Such chirality (see Fig. 1.5b) may occur for any type of overlayer lattice apart from the oblique type (for which lattice chirality is intrinsic).

**Planar Substrate Chirality**
Chirality associated with the arrangement of substrate atoms across a two-dimensional facet (which may or may not lie parallel to the macroscopic surface plane). Such chirality is dictated only by the orientation of the facet and the three-dimensional structure of the parent bulk material (see Chapter 2).

**Linear Substrate Chirality**
Chirality associated with the arrangement of substrate atoms along a one-dimensional line where two facets meet (either along a ridge or a furrow). Such chirality is dictated only by the orientations of the two facets and the three-dimensional structure of the parent bulk material (see Section 3.6.1).
**Pointlike Substrate Chirality**

Chirality associated with the arrangement of substrate atoms at a zero-dimensional point where three facets meet (either at the apex of a pyramid or the bottom of a pit). Such chirality is dictated only by the orientations of the three facets and the three-dimensional structure of the parent bulk material (see Section 3.6.2).

### 1.5 Diastereoisomerism Defined

The categorisation of surface chirality introduced in the preceding section makes it clear that a given system may, taken as a whole, display chirality in multiple aspects simultaneously. Throughout this book, we shall be interested in situations where the combination of two chiral aspects results in an *enantiospecific* outcome, defined as one that distinguishes in some way between the two different enantiomers of one of these chiral aspects. This already rather general concept may, in turn, be further generalised by considering the labelling of chiral entities in the most abstract sense.

Let us imagine, therefore, that some particular system displays chirality in two distinct aspects. These might be, for instance, planar substrate chirality and irreducible molecular chirality, but for our present purpose we need only recognise them as separate from one another and keep track of their chiral labels independently. If each chiral aspect is individually labelled either D or L, then the four possible combinations may be listed as DD, LL, DL and LD, where the first-listed symbol should be taken to label the chirality of the first chiral aspect of the system, and the second-listed symbol to perform the same function for the second. Clearly, the combinations labelled DD and LL are precise enantiomers of one another and must therefore represent degenerate situations; similarly, the DL and LD combinations form another degenerate enantiomeric pair of situations. It is evident, however, that the DD and LL combinations are related to neither the DL nor the LD combination by mirror symmetry. This type of non-degenerate and non-enantiomeric relationship is said to be **diastereomeric** in nature, and the entire pattern of enantiomeric and diastereomeric pairs (Fig. 1.6) constitutes

![Pattern of diastereoisomerism](image)

**Figure 1.6** Pattern of diastereoisomerism, whereby DL and LD combinations form a degenerate enantiomeric pair, as do DD and LL combinations. In contrast, DL and DD combinations form a non-degenerate diastereomeric pair, as do the LD and LL combinations.

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6 Strictly speaking, the more restrictive term ‘enantioselective’ (previously defined) only really applies to the concept of enantiospecificity in the context of chemical reaction rates.
the phenomenon of diastereoisomerism. The origin of all enantiospecificity lies in the diastereomeric difference pertaining to some property of the system in question – purely enantiomeric differences are discernable only by other chiral systems, whereas diastereomeric differences are relevant to all manner of properties that are not themselves inherently chiral, such as thermodynamic and/or kinetic parameters.

1.6 Quantifying Chirality?

Defined as the absence of improper symmetry elements, the state of being chiral is absolutely binary. It is no more possible to be ‘a little bit chiral’ than it is to be ‘a little bit pregnant’. An entity is either chiral or it is not, and it ought therefore to be readily apparent that any effort to quantify the degree of chirality such an entity possesses must surely be doomed to failure – or at least ambiguity. This consideration has not, however, prevented a number of authors from proposing ‘figures of merit’ that purport to reveal how chiral an object might be. At best, these quantities may correlate with some aspect of chirality, but considerable caution should be exercised in their interpretation.

The essential point to grasp is this: while it is true that a particular chiral entity may behave as if it is ‘more chiral’ than another, according to the outcome of some specific type of experiment, it is always possible that the apparent ‘order of chirality’ may be reversed when studied via some other type of experiment. It is only ever possible to gauge the ‘degree of chirality’ in terms of the system’s diastereomeric response to some well-defined ‘probe of chirality’. To give a concrete example, consider two entirely different species whose degree of chirality is first assigned by means of their optical rotary power (i.e. their ability to rotate the linear polarisation vector of light in transmission); let us suppose that we test enantiopure samples of each species that happen to rotate the polarisation vector in the same sense, and naively insist that the species with the higher optical rotary power is somehow ‘more chiral’ than the other. If the same two species are subsequently tested as to their ability to act as asymmetric catalysts in some particular reaction, there is absolutely no reason to suppose that the species with the greater optical rotary power will be more effective in producing an excess in one of the product enantiomers over the other; indeed, there is no reason a priori to suppose that the two species will produce asymmetry amongst the products in the same sense as each other, despite their optical rotations being in the same sense. It is clear, therefore, that

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7 We have already come across one example of this type of chiral combinatronics in the case of molecules possessing two chiral centres (see Section 1.3) where we noted that the \( R,R \) and \( S,S \) forms were enantiomers of one another but distinct from \( K,S \) and \( S,R \) forms that constitute a second enantiomeric pair.

8 Harris et al. have rigorously confirmed this principle within the framework of group theory, showing that not only may there be infinitely many chiral parameters that characterise a single chiral system equally well, but also that these parameters can vary independently of one another under a continuous deformation of that system. Indeed, it is even possible for a particular parameter to switch sign independently of all the others, so that the apparent handedness of a system may swap from the viewpoint of one probe, but not from that of another!
the ‘quantity’ and ‘sign’ of chirality differs between physical and chemical probes of the chirality, according to the diastereoisomerism exhibited by the chirality of the sample coupled with that of the probe. And that is even without considering that one might devise more than one type of physical probe (based, for example, on stress or magnetism) and more than one type of chemical probe (based on a different chemical reaction). The quantification of chirality by means of a particular chiral probe is of use only in the context of that specific probe, and hence is of no practical use whatsoever in predicting behaviour in other contexts.

For the reasons outlined above, there have been a few efforts to devise schemes for quantifying chirality based upon geometric considerations alone. These efforts miss the point, however, since they may equally be considered (in an abstract sense) as tests of chirality based not upon a physical or chemical probe but upon a geometric probe. It is, of course, entirely possible to define geometric tests to quantify the extent to which one enantiomer differs from its mirror image, but there is no reason to suppose that any scale of chirality based upon such a test should have any bearing upon the behaviour of those enantiomers when subjected to asymmetric physical or chemical stimuli. Even restricting ourselves entirely to the realm of geometry, inconsistency is bound to arise, as may be seen by extending the classic example of hands and gloves to include feet and shoes.

The origin of asymmetric response in chiral systems is often illustrated by means of analogy with the idea of fitting hands into gloves.9 Imagine that a left hand and a right hand correspond to the two enantiomers of a chiral species. So long as those two hands experience only non-chiral environments, their behaviours will be indistinguishable. Tasked with catching a spherical ball, for instance, either hand can do so equally well. Faced with a chiral environment, however, the two hands may be readily distinguished. If provided with a right-handed glove, for example, the right hand will be able to slip inside easily, whereas the left hand will not. This much is obvious, and implies that the ‘glove-shaped’ geometric probe registers the hands as being ‘very chiral’ (i.e. the diastereomeric difference in geometry for the hand–glove system is large). Extending the analogy to include feet, one imagines a left foot and a right foot, equally capable of kicking a spherical ball, but only the right foot will slip easily into a right-footed shoe. Here, the ‘shoe-shaped’ geometric probe registers the feet as being ‘very chiral’ (i.e. the diastereomeric difference in geometry for the foot–shoe system is large).

The ambiguity of this approach is revealed, however, when the ‘shoe-shaped’ geometric probe is used to test the chirality of hands; here, both hands will fit into a right-footed shoe with approximately equal ease – the probe will register the hands as being only ‘slightly chiral’ (i.e. the diastereomeric difference in geometry for the hand–shoe system is small). Similarly, if the ‘glove-shaped’ geometric probe is used to test the chirality of feet, both feet will fit into a right-handed glove almost equally badly – the probe will register the feet as being only ‘slightly chiral’ (i.e. the diastereomeric difference in geometry for the foot–glove system is small). The moral of the story is that there is no such thing as an absolute quantitative measure of chirality, even when restricting oneself to

9 See the preface to this book.
the realm of pure geometry, let alone when concerned with physical or chemical phenomena. Chirality simply appears to be strong when the probe that is in use happens to match, in some sense, the nature of the chiral entities under test. It is quite possible for an object to yield a very strong asymmetric response under one set of circumstances, despite showing only a very weak asymmetric response under another. In this book, we shall endeavour to refrain from making absolute statements about the degree of chirality evident at a surface, as opposed to specific statements about the asymmetry of response to a specific situation, reflected in the diastereomeric difference of some quantity of interest.

1.7 Enantiomeric Excess

Notwithstanding the admonition of the preceding section, there is at least one aspect in which chirality can be meaningfully quantified: when a mixture of chiral entities is present, one may sensibly express the dominance of one or the other enantiomer by means of that quantity known as the enantiomeric excess. Given the symbol $ee$, the enantiomeric excess is defined as

$$ee = \frac{N(+) - N(-)}{N(+) + N(-)} \quad (1.2)$$

where $N(\cdot)$ are, respectively, the number of dextrorotary and laevorotary entities (or number of moles of such entities) present in the mixture. Despite arguments [8, 9] that this definition introduces needless complexities that would be avoided by use of a simple enantiomeric ratio (i.e. $er = N(\cdot)/N(\cdot)$) the enantiomeric excess remains the de facto standard for quantifying the asymmetry of chiral mixtures.10 We note here two special cases, namely: (i) the so-called racemic case, where the enantiomeric excess is precisely zero, and (ii) the enantiopure case, where the enantiomeric excess is either plus or minus unity. A sample with arbitrary enantiomeric excess can always be obtained by combining a racemate (i.e. a racemic mixture) with an appropriate quantity of enantiopure material.

Extending the concept from the description of chiral entities to the description of chiral processes, we can define an enantiomeric excess in the rates of a reaction. That is, we specify

$$ee_r = \frac{r\| - r\perp}{r\| + r\perp} \quad (1.3)$$

where we shall take $r\|$ to be the rate when the reaction takes place between entities whose chiral labels (i.e. D or L) happen to match, and $r\perp$ to be the rate when the chiral labels do not match. The $\|$ and $\perp$ symbols thus identify the two non-degenerate states of the diastereomeric situation; positive values of $ee_r$ imply that the reaction occurs fastest when the chiral labels of the involved entities match, while negative values would imply a faster reaction when they differ.

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10 It is, of course, essentially trivial to convert between enantiomeric excess and enantiomeric ratio. The necessary equations are simply $ee = (er - 1)/(er + 1)$ and $er = (1 + ee)/(1 - ee)$. 
Furthermore, we may write these rates as
\[ r_\parallel = k_\parallel f_\parallel \] (1.4)
and
\[ r_\perp = k_\perp f_\perp \] (1.5)
where \( k_\parallel \) and \( k_\perp \) are rate ‘constants’ varying only with temperature, and where \( f_\parallel \) and \( f_\perp \) are functions representing all other aspects of the current state of the system; in the context of a gas-phase reaction, these latter functions will, in general, depend upon the concentrations of any reactants; for a surface reaction, the relevant variables may be the coverage of reactants and/or the areal density of active sites. With these definitions in mind, we may now introduce the quantity
\[ ee_k = \frac{k_\parallel - k_\perp}{k_\parallel + k_\perp} \] (1.6)
which we shall term the **enantiomeric excess in the rate constants**. Note that this last quantity must be carefully distinguished from the enantiomeric excess in the rates – identical rate constants may give rise to rather different actual rates depending upon the current coverages and/or availability of active sites.

Now, rate constants for activated processes can generally be written in the form
\[ k = ve^{-E/k_BT} \] (1.7)
and doing so in the preceding expression yields
\[ ee_k = \frac{v_\parallel e^\alpha - v_\perp e^{-\alpha}}{v_\parallel e^\alpha + v_\perp e^{-\alpha}} \] (1.8)
with
\[ \alpha = (E_\perp - E_\parallel)/2k_BT \] (1.9)
where \( E_\parallel \) and \( E_\perp \) are the activation energies, \( v_\parallel \) and \( v_\perp \) the corresponding pre-exponential factors, \( k_B \) the Boltzmann constant and \( T \) the temperature.

If we make the assumption that the pre-exponential factors are not sensitive to chirality (i.e. \( v_\parallel = v_\perp \)) this reduces to the simple form
\[ ee_k = \tanh \alpha \] (1.10)
which varies monotonically from plus or minus unity at absolute zero temperature to zero at infinite temperature. In fact, the same is equally true for the general expression also.\(^{11}\) We should, however, stress that no such simple behaviour may be inferred for the enantiomeric excess in the rates, for the reason alluded to above – the rates are a product of the rate constants with functions expressing the current state of the system, and these latter will, in turn, depend upon

\(^{11}\) Differentiating Eq. (1.6) with respect to temperature and setting the result to zero, one finds \( k_\parallel k_\parallel' = k_\perp k_\perp' \) (where primed quantities represent temperature derivatives) as the criterion for a stationary value of \( ee_k \). Making use of Eq. (1.7), it becomes clear that this criterion is satisfied only in the trivial case where the activation energies \( E_\parallel \) and \( E_\perp \) are equal. In all other cases, the enantiomeric excess in the rate constants can have no stationary values and must, therefore, vary monotonically. Since the values at absolute zero and infinite temperatures may readily be shown to be unity and zero, the statement in the text is proved.
the history of the system. In comparing the enantiomeric excess in the rates, it matters greatly whether a given experiment is performed, for example, at constant temperature or at constant rate of temperature change.

Finally, we note that all three of these enantiomeric excess quantities may be recast in percentage form, namely, \( \%ee = ee \times 100\% \) and similar expressions for \( \%ee_r \) and \( \%ee_k \). In this form, the range of each is transformed to \( \pm 100\% \), and the racemic situation corresponds to a value of 0%.

### 1.8 Synthesis, Separation and Sensing

To conclude this introduction, let us reflect that whilst studying chiral systems may be intellectually stimulating in its own right, the true test of our mastery of any subject lies in our ability to make use of it for predefined ends. If we truly understand it, we ought to be able to apply it. From the standpoint of chemistry, at least, three target applications for surface chirality may readily be identified and summarised as follows:

**Asymmetric Synthesis**

Ideally, one could imagine a heterogeneous analogue of the catalytic processes currently carried out in the homogeneous realm, where chiral catalysts skew the product distribution of a particular reaction to favour a marked excess of one enantiomer over its mirror image. The advantage over a homogeneous catalytic reaction would be the ability to run continuously, rather than in batch mode, but the major challenge lies in achieving a sufficiently high enantiomeric excess. Applications for chiral molecules (e.g. in the pharmaceutical industry) typically require very high levels of enantiomeric purity, so if asymmetric synthesis alone is to be relied upon its selectivity must be extreme.

**Asymmetric Separation**

Failing to synthesise a particular chiral product with sufficient enantioselectivity, one might resort to post hoc separation of a racemic (or even just slightly enantio-impure) mixture. Again, this can already be achieved by homogeneous means, but the efficiencies of heterogeneous processing are very attractive. The essence of asymmetric separation lies in binding one enantiomer in excess over the other, but in addition to the inherent requirement for extreme selectivity, a further challenge lies in the need to avoid poisoning the adsorbent; an ideal solution might hypothetically be found in a switchable system capable of binding first one enantiomer and then the other, so that temporal cycling can be employed to maintain an active surface.

**Asymmetric Sensing**

Under this heading, one imagines a device capable of responding to the chemical asymmetry of two enantiomers by changing some readily measurable physical property. For example, such a device might respond to an enantiomeric excess by exhibiting a proportional (or at least monotonic) change of reflectivity, magnetism or conductivity. In this way, it would be possible to monitor the chiral composition of a flowing product stream in real time, confirming that asymmetric synthesis or separation processes are achieving the desired enantiomeric excess.
References