

Chemical Group Theory

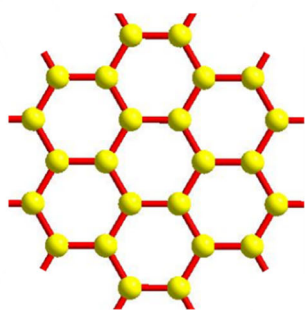
II. Symmetry in Crystalline Solids

(Notes to accompany the lectures in CHEM 583)

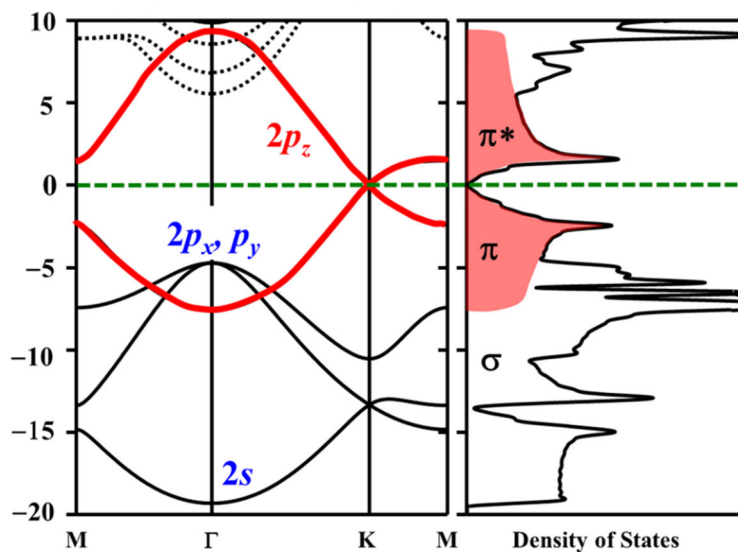
Gordon J. Miller

Department of Chemistry

Iowa State University



Graphene
p6mm



SYMMETRY IN CRYSTALLINE SOLIDS

This collection of notes is arranged according to the slides presented during lectures and provides some additional perspectives on the material.

OUTLINE: *Group theory* provides the mathematical framework for applying the symmetry of a chemical structure to characterize its various physical states and properties. Therefore, this section of the course is divided into two subsections:

STRUCTURAL SYMMETRY OF CRYSTALS

- 1) Translational Symmetry: Lattice concept; translation group characteristics and features; periodic boundary conditions; unit cells
- 2) Rotational Symmetry: International notation for point groups; compatibility of rotations and translations; crystallographic point groups; Bravais lattices
- 3) Space Groups: Rotation-translation operations; screw rotations/glide reflections; interpreting space group symbols; symmorphic vs. nonsymmorphic groups; subgroups

ELECTRONIC AND VIBRATIONAL STATES OF CRYSTALS

- 4) Reciprocal Space: Periodic functions and the reciprocal lattice; irreducible representations of the translation group for 1-dimension and generally
- 5) Bloch's Theorem: Properties of wavefunctions under periodic potentials; Brillouin zones; Bloch functions; electronic and vibrational states for a 1-dimensional crystal
- 6) Irreducible Representations of Space Groups: Relationships between wavevector and rotational symmetry; π electronic structure of graphene

RESOURCES: There are numerous resources covering the subject of group theory applied to chemistry and physics, so please perform your own on-line searches or browse the ISU library for the various topics we will cover during this section of the course.

ON-LINE RESOURCES:

Bilbao Crystallographic Server (<https://www.cryst.ehu.es>)

A comprehensive resource for widespread applications of space groups; initiated in 1997 at the Materials Laboratory of the University of the Basque Country, Spain.

International Tables for Crystallography (<https://it.iucr.org>)

A multi-volume set of encyclopedic resources for crystallography; Volume A thoroughly covers two-dimensional plane groups and 3-dimensional space groups – NOTE: use 2006 Edition from the Iowa State University campus.

MONOGRAPHS:

Space Groups for Solid State Scientists, 3rd Edition, G. Burns and A.M. Glazer, Academic Press, San Diego, 2013 (QC176 .B865 2013); Online access via ISU Library website

Structural symmetry with little mathematical formalism but many black-and-white figures; descriptive style of writing; provides information on how to read and interpret the *International Tables for Crystallography, Volume A*.

Physical Chemistry of Solids, H.F. Franzen, World Scientific, Singapore, 1994 (QD478 .F73 1994); Online access via ISU Library website

Group theory for solids is about one-half of the material; mix of formalism and applications; problems at the end of each chapter with solutions as an appendix.

Applied Group Theory for Chemists, Physicists, and Engineers, A. Nussbaum, Prentice-Hall, Englewood Hills, NJ, 1971 (QD461 .N85)

Brings together group theory for molecules and crystalline solids; nice summary/comparison of notations for point groups; many worked out examples in the midst of descriptions; covers structural aspects and electronic structure.

ADDITIONAL REFERENCES:

Induced Representations in Crystals and Molecules, S.L. Altmann, Academic Press, London, 1977 (QD911 .A47)

Mathematical treatment of determining irreducible representations for space groups and nonrigid molecules.

The Mathematical Theory of Symmetry in Solids, C.J. Bradley and A.P. Cracknell, Clarendon Press, Oxford, 1972 (QC176 B65 2010); Online access via ISU Library website

Complete theory of the irreducible representations of the crystallographic point groups and space groups accompanied by extensive tables.

Elementary Crystallography; An Introduction to the Fundamental Geometrical Features of Crystals, M.J. Buerger, Wiley, New York, 1956 (QD905 .B862e); 3rd Printing 1965 – Full text available via ISU Library website

Broad and detailed geometrical narrative on crystallographic point groups and 3d space groups; derives the 230 3d space groups systematically although the reader must become familiar with Buerger's notation.

Group Theory and Electronic Energy Bands in Solids, J.F. Cornwell, North-Holland, Amsterdam, 1969 (QC174.5 C57)

Mathematical treatment of determining irreducible representations for space groups and their applications to free-electron energy band structures.

Group Theory and Its Application to Physical Problems, M. Hamermesh, Addison-Wesley, Reading, MA, 2nd Printing, 1964 (Published by Dover, 1989: QA171 .H28 1989)

“Gold standard” of an extensive mathematical discussion of group theory for various problems involving atoms, molecules, and other chemical systems.

Crystallographic Groups, T. Janssen, North-Holland, Amsterdam, 1973 (QD905.2 .J36)

Succinct but thorough narrative on groups applied to crystals.

Symmetry Principles in Solid State and Molecular Physics, M. Lax, Dover, Mineola, NY, 2001 (QC174.5 .L38)

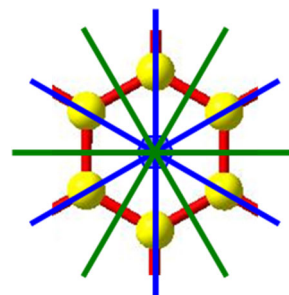
Another complementary mathematical treatment of group theoretical principles to solid-state problems.

Crystal Properties Via Group Theory, A.S. Nowick, Cambridge University Press, Cambridge, 1995 (QD911 .N67 1995)

Application of group theory to tensorial properties of crystals and crystalline properties.

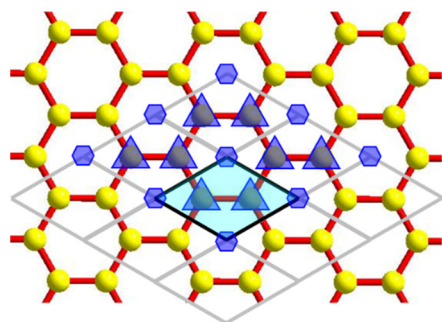
OVERVIEW

(1) Crystalline Structures: Identifying the structural symmetry of molecules and solids is important to understand the nature of their physical and some chemical properties. Molecular symmetry is summarized by a *point group*, for which all symmetry elements (points, axes, planes) intersect at one fixed point that is assigned as the origin of the spatial coordinate system. For example, consider benzene with point group D_{6h} . The origin lies at the center of the molecule where there is no atom. Some of its symmetry elements include a six-fold rotation axis and six vertical mirror planes; the corresponding operations are rotations by multiples of $2\pi/6$ (60°) and reflections.

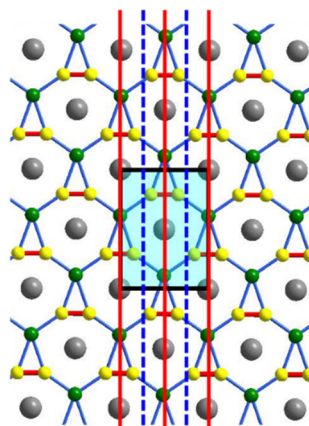


Benzene molecule

Crystalline solids, on the other hand, display rotational symmetry at multiple points in space because these structures also exhibit translational periodicity, which is described by a lattice. The combination of rotational and translational symmetry operations yields a *space group*. Consider the structure of graphene, which consists of a planar network of fused six-membered rings of carbon atoms. If termination of the structure in the plane is ignored, then there are six-fold rotation axes at the centers of every hexagon, and each carbon atom intersects a three-fold rotation axis. The translational periodicity is represented by unit cells (parallelograms) that connect the centers of every hexagon. As another example, the structure of $CeNiC_2$ contains $[NiC_2]$ planes alternating with planes of Ce atoms that sit above and below seven-membered rings of the $[NiC_2]$ planes. In the projection of this structure along the stacking direction, a unit cell is a rectangle and vertical mirror planes are apparent. Moreover, there is another type of symmetry operation for this crystalline structure that does not occur for any molecule: glide reflections, in which a reflection through a mirror plane is followed by a displacement parallel to (“gliding along”) the reflection plane. Neither the reflection on its own nor the displacement on its own is a symmetry operation, but the combination of the two operations is for the $CeNiC_2$ structure.



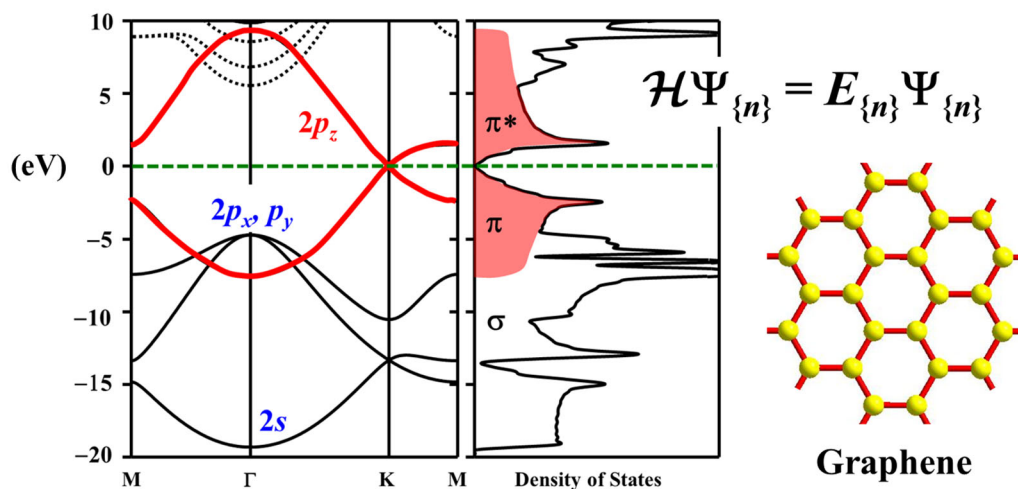
Graphite (Graphene)

 $CeNiC_2$

(Left) Graphene structure showing diamond-shaped unit cells, as well as six-fold and three-fold rotational symmetry axes.

(Right) $CeNiC_2$ structure (Ce: dark gray; Ni: green; C: yellow) showing a rectangular unit cell, vertical reflection planes (red), and glide planes (blue dashed).

(2) **Electronic Structures:** The symmetry of atomic structures gives insights into the qualitative features of electronic states, their degeneracies, and allowed or forbidden electronic transitions between states. A thorough understanding of electronic states of crystalline structures requires determining the *irreducible representations* of the space group. Electronic states may be deduced from spectroscopic measurements or calculated by solving Schrödinger's equation. The results of these computations for a crystalline solid like graphene are illustrated by *energy band diagrams* and *density of states* plots. Energy band diagrams show individual crystal orbital energies plotted as functions of wavevectors, which are quantities related to the translational symmetry. Electronic density of states diagrams illustrate the relative numbers of electronic states vs. energy and are the solid-state analogues of molecular orbital energy diagrams.



Calculated valence electronic structure for graphene.