

Chemical
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and
Spectroscopy
in
Mineral
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EDITED BY

Frank J. Berry

and

David J. Vaughan

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Preface

In recent years mineralogy has developed even stronger links with solid-state chemistry and physics and these developments have been accompanied by a trend towards further quantification in the theoretical as well as the experimental aspects of the subject.

The importance of solid-state chemistry to mineralogy was reflected in a symposium held at the 1982 Annual Congress of The Royal Society of Chemistry at which the original versions of most of the contributions to this book were presented. The meeting brought together chemists, geologists and mineralogists all of whom were interested in the application of modern spectroscopic techniques to the study of bonding in minerals. The interdisciplinary nature of the symposium enabled a beneficial exchange of information from the various fields and it was felt that a book presenting reviews of the key areas of the subject would be a useful addition to both the chemical and mineralogical literature.

The field of study which is commonly termed the 'physics and chemistry of minerals' has itself developed very rapidly over recent years. Such rapid development has resulted in many chemists, geologists, geochemists and mineralogists being less familiar than they might wish with the techniques currently available. Central to this field is an understanding of chemical bonding or 'electronic structure' in minerals which has been developed both theoretically and by the use of spectroscopic techniques. The purpose of this book is to outline the fundamental concepts associated with current models of bonding and to serve as an introduction to the techniques which may be applied in this area of mineral chemistry. It is not the intention of the text to provide a laboratory manual for the techniques discussed, neither is it intended that reviews of the literature detailing applications be comprehensive. This book is a starting point from which the interested reader can progress to many of the more detailed accounts cited in the various chapters.

The book begins with a chapter on the use of quantum mechanics in producing models of chemical bonding in minerals. The next two chapters

consider the application of X-ray spectroscopy and of electronic absorption spectroscopy and are followed by a chapter on the more specialist technique of luminescence spectroscopy. All of these methods involve the interaction of some form of electromagnetic radiation with the electrons in solids and provide information about the energies and distributions of the electrons. The next two chapters deal largely with the interaction of radiation with atomic nuclei in minerals as in Mössbauer spectroscopy and nuclear magnetic resonance. These techniques generally serve as more indirect, although equally powerful, probes of the electronic structures of solids. The last two chapters deal with the special problems, as regards both theory and experiment, which are posed by opaque minerals and with the applications of spectroscopic methods for the elucidation of the surface properties of minerals.

If the readers of this book are consequently led to look more deeply into the fascinating areas of bonding and spectroscopy in mineral chemistry then our objectives will have been achieved.

F.J. Berry
D.J. Vaughan
Birmingham, 1984

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Quantum Mechanical Models and Methods in Mineralogy

J.A. Tossell

1.1 INTRODUCTION

In this chapter I will discuss the rather brief history of the application of quantum mechanical methods to mineralogical problems. I will first consider the modelling and methodological aspects of the problem and then give a number of examples of recent quantum mechanical studies of crystal structures, spectra and valence electron densities in minerals. In addition to results of quantum mechanical computations I will discuss some recent qualitative molecular orbital (MO) interpretations of mineral properties. Finally, I will indicate future productive directions for quantum mineralogical studies and suggest the role that different scientists can play in advancing quantum mineralogy.

We should first note that mineralogy is usually defined as 'the study of naturally occurring inorganic crystalline solids', a specific and rather limited subset of matter. The employment of theories and experimental techniques which have reached maturity in mathematics, chemistry and physics is common in the history of mineralogy. The utilization of quantum mechanics in mineralogy is just another example of such a transference of technique from a more basic to a more applied area. As I will show, quantum mechanics can give information useful for interpreting or simulating the crystal structure, physical properties and (to some extent) phase equilibria of minerals. It also provides the appropriate formalism for understanding almost all mineral spectral properties.

Quantum mineralogy is quite young, its development being roughly ten years behind that of quantum chemistry. Thus, we are still exploiting techniques in quantum mineralogy developed by quantum chemists in the early 1970s. In the qualitative applications of quantum theory mineralogists are even further behind chemists. Some significant books whose publication dates illustrate these points are listed in Table 1.1. Note that I have listed an early book on qualitative bonding theory by Fyfe.¹ This was a sound book but was unsuccessful in modifying the attitudes of mineralogists since the qualitative valence bond and MO ideas used could rationalize mineral properties no better than the dominant ionic model and were unfamiliar to most mineralogists.

The first quantitative MO studies which focused specifically on minerals were by Gibbs' group² employing extended Hückel MO theory to correlate bond distance and angle variations with Mulliken overlap populations, and my own^{3,4} using approximate self-consistent-field linear combination of atomic orbitals (SCF-LCAO) and multiple scattering $X\alpha$ (MS- $X\alpha^5$) MO methods to interpret mineral X-ray spectral data. Much more accurate calculations have since been performed which support the qualitative conclusions of the original studies. We continue to generally employ Hartree-Fock based methods for structural studies and MS- $X\alpha$ methods for spectral studies. Much of this work has been previously reviewed.⁶⁻⁸

As quantum mineralogy has matured it has developed a number of distinct areas. Theoretical studies using both large-scale computation and more qualitative approaches have proved valuable. In the experimental area, early emphasis upon properties previously interpreted by the classical ionic model, such as bond distances and angles, has been replaced by study of intrinsically quantum mechanical properties such as spectra, and properties showing clearly the limitations of the ionic model, such as valence electron density distributions.

Table 1.1 Comparison of publication dates of books on quantum chemistry and quantum mineralogy

	Chemistry	Mineralogy
First book using crystal field theory	1960 (Griffith, ⁶⁹ Orgel ⁷⁰)	1970 (Burns ⁷¹)
First book using qualitative MO theory	1962-1965 (Roberts, ⁷² Ballhausen and Gray ⁷³)	1964 (Fyfe ¹) 1978 (Vaughan and Craig ⁷⁴) 1980 (Burdett ⁶¹)
First book on quantitative MO computations	1972 (Schaefer ¹¹)	Not yet!

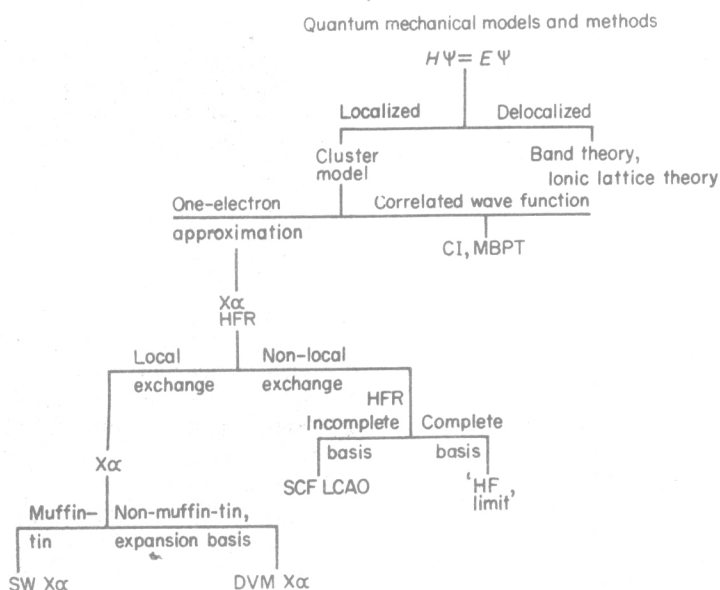


Fig. 1.1 Choices of physical model and computational method for quantum mineralogical studies.

In applying quantum mechanics to minerals, we face two distinguishable difficulties, which I will formulate as choices of 'model' and 'method'. A flow chart indicating required choices of model and method is shown in Fig. 1.1. What physical model will we use - a delocalized one, treating the whole periodic solid as in ionic lattice theory and band theory, or a localized molecular cluster approach? Although I will mention some interesting results of band theoretical and ionic lattice calculations, I will focus on the localized cluster approach which we have found to usefully describe a wide range of solid properties.

Once our physical model has been chosen we must pick a particular quantum mechanical method. All of the results which I shall discuss employ the independent electron approximation, in which each electron is assumed to move in a potential field produced by the nuclei and the averaged charge density of the other electrons. This approximation allows us to write the wavefunction for a system containing n electrons as an antisymmetric product of functions dependent upon the coordinates of one electron only. Antisymmetry is required so that the wavefunction satisfies the Pauli exclusion principle. However, such a wavefunction does not properly describe the correlation in the motion of electrons, i.e. the fact that the motion of one electron depends on the instantaneous positions of the other electrons, not

simply on the charge density. This deficiency may be remedied by the techniques of configuration interaction (CI) or perturbation theory but no such calculations have yet been carried out for mineral systems. The total energy of the systems may be obtained as the quantum mechanical average value over the ground state wavefunction of the Hamiltonian operator. The most difficult terms to calculate in the Hamiltonian are those describing the electron–electron repulsions, particularly the ‘exchange’ terms arising from the antisymmetry requirement. To calculate the exchange contribution to the total energy we may employ the matrix Hartree–Fock or Hartree–Fock–Roothaan⁹ method in which each one electron orbital is expanded as a linear combination of simple analytical functions, usually centred on the nuclei. The exchange energy can then be decomposed into a sum of integrals whose number increases as the fourth power of the number of expansion functions used. Alternatively, the exchange energy may be approximated as proportional to the one-third power of the total electron density at a point.¹⁰ Although less accurate in theory than the Hartree–Fock method such local exchange or X_α or Hartree–Fock–Slater methods produce great computational savings and yield accurate results. Hartree–Fock–Roothaan (HFR) calculations can be further characterized by the size of the expansion basis set used (see Schafer¹¹ for a discussion of HFR calculations). An effectively infinite basis set is needed to obtain the true Hartree–Fock wavefunction. However, since the difficulty of the computation increases as the fourth power of the basis set size HFR calculation on most mineral model systems have employed either a minimal basis (one expansion function for each atomic orbital occupied in the free atoms from which the molecular system is formed) or a split valence basis (two expansion functions per occupied atomic valence orbital). X_α calculations may also be done with expansion basis sets¹² but most of the calculations I will describe use the muffin-tin scattered wave procedure of Johnson.⁵ In this method the space of the molecular cluster is partitioned into regions and the quantum mechanical potential is simplified by various averaging procedures within these regions. Schrödinger’s equation can then be solved separately in the various regions. Continuity of the wavefunction and its first derivative at the boundaries of the different regions is then required to obtain a wavefunction acceptable over all space. Although such a muffin-tin averaging procedure reduces the accuracy of the potential it makes possible a very efficient multiple scattering expansion of the wavefunction, resulting in a dramatic savings in computer time (see Appendix to Tossell and Gibbs⁶).

Thus, the calculations described herein will be quite crude by the standards of small molecule quantum chemistry. Independent electron calculations which employ large expansion basis sets (split valence plus polarization functions) and include electron correlation by configuration interaction or perturbation theory can reproduce bond distances and angles for small molecules to within experimental accuracy.¹³ Such accuracy cannot be expected in quantum mineralogical studies since the large size of the mineral

model systems prohibits the use of large expansion basis sets and since the approximations inherent within the molecular cluster model for a solid remain, no matter how accurate the cluster wavefunction. An inspection of the recent literature indicates that cluster models of solids are now used by a number of different groups, including solid state physics theoreticians^{14,15} and theoretical chemists interested in surface properties¹⁶ (see also Chapter 8 of this book), both of whom have addressed the questions of choice of cluster size and boundary conditions (to which we return later in this chapter).

1.2 FULL LATTICE CALCULATIONS

Let me first mention some results using the full lattice approach for a simple compound (MgO) with few electrons and high symmetry, and which is of some interest mineralogically. MgO is of interest partly because silicate minerals such as olivine break down to mixed magnesium-iron oxide and silicon dioxide (in the 6-coordinate stishovite form) at high pressures. Phase transitions in this material at high pressure were studied¹⁷ using the full lattice modified electron gas (MEG) ionic model,¹⁸ which evaluates the energy of an ion pair by assuming the total density to be the sum of the free ion densities, and by using energy expressions appropriate to an electron gas of uniform density. Previous studies on alkali halides by this method yielded reasonable phase transition pressures (Table 1.2). The method may be made purely non-empirical by calculating the anion wavefunction within a self-consistent stabilizing potential,¹⁹ although early studies used free anion wavefunctions with arbitrary stabilizations. The method yielded a predicted pressure for transformation of NaCl(B1) structure MgO to the CsCl(B2) polymorph of $\sim 2560 \times 10^3$ atmospheres, which is considerably above pressures in the Earth's mantle in which MgO might occur. Even though transition pressures are very hard to predict accurately, this result suggests strongly that only NaCl structure MgO exists in the Earth.

Experimental studies by two groups on pure MgO have shown metallic conductivity at about 1 Mbar. However, two separate band calculations^{20,21} indicate the MgO band gap will first increase with pressure and only become

Table 1.2 Calculated and experimental pressures (kbar) for 6→8 coordinate phase transitions in alkali halides and MgO (Cohen and Gordon¹⁷)

Compound	Calculated	Experimental
LiCl	908	7100
NaCl	107	300
RbCl	17	5.5
MgO	2560	—

Table 1.3 Calculated and experimental phase transition pressures from MEG calculations on dihalides and dioxides (Tossell²⁴)

Compound and coordination numbers of transition polymorphs	Pressure (kbar)	
	Calculated	Experimental
MgF ₂ 6→8	200–420	330
SiO ₂ 4→6	125	75
SiO ₂ 6→8	3.9×10^3	—
TiO ₂ 6→8	8.3×10^2	—

zero at ~ 50 Mbar. Although the experimental data may be erroneous, it may well be that the conductive material observed is not perfectly stoichiometric single crystal MgO, but rather some reaction product, perhaps containing peroxide groups.²² Such band theoretical studies on perfect materials may, therefore, be of limited relevance to real minerals. Nonetheless, the results of Bukowinski²⁰ on MgO are certainly interesting in themselves. They indicate a considerable delocalization of electron density at high pressure in MgO, reducing its 'ionic' character. Even more interesting results²³ are obtained for materials such as CaO and K at high pressure, since d-like electronic states are stabilized relative to s states leading to an electronic structure much like that of an atmospheric pressure transition metal for the K case.

My own MEG studies on more complex materials²⁴ indicate that structures and energies are described well for alkaline earth dihalides and somewhat less accurately for dioxides, such as SiO₂. Such studies give reasonable phase transition pressures (Table 1.3) and indicate that SiO₂ will not transform from the 6-coordinate stishovite structure to the 8-coordinate CaF₂ structure hypothesized within the Earth's mantle. Therefore, although accurate prediction of transformation pressures is very difficult, present methods can at least place some constraints upon expected high pressure behaviour. Catlow and Cormack²⁵ have also done interesting ionic lattice calculations using empirical ion-pair potentials. Although such semi-empirical studies can give us little direct information on the nature of bonding in solids they can accurately simulate the properties of both perfect and disordered solids which have interatomic interactions similar to those of the solids employed for the parametrization. For example, Catlow *et al.*²⁶ have recently predicted with reasonable accuracy how the preferred structure-type for chain silicates varies with cation identity, or cation-oxygen bond distance.

1.3 CLUSTER CALCULATIONS ON MINERAL STRUCTURAL PROPERTIES

Let me now turn to the application of cluster models in mineralogy. For some solids, definition of an appropriate cluster seems intuitively straightforward.

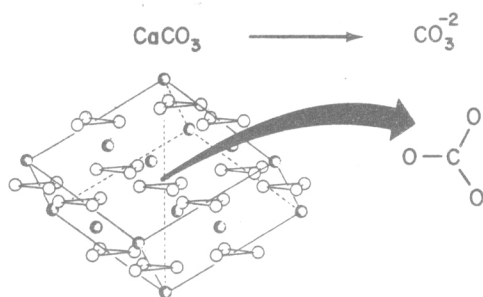


Fig. 1.2 CO_3^{2-} cluster abstracted from CaCO_3 .

Table 1.4 Calculated and experimental C–O distances and A_1 vibrational frequencies in carbonates

	C–O distance(\AA)	ν_{A1} (cm^{-1})
Free CO_3^{2-} minimum basis	1.327, 1.330	1105
split valence basis	1.305	–
CO_3^{2-} in charge array, minimum basis	1.332	1064
CaCO_3 , exp.	1.294	1082
all carbonates, experimental	1.27–1.31	–

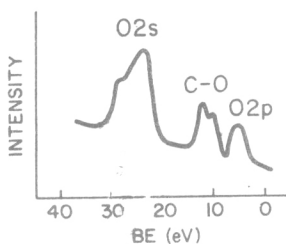


Fig. 1.3 X-ray spectra of K_2CO_3 .

For example, we might describe CaCO_3 as a collection of discrete CO_3^{2-} and Ca^{2+} ions held together by weak ionic bonds, and detailed calculations indicate that many carbonate properties can be understood by focusing on CO_3^{2-} alone (Fig. 1.2). Rather crude HFR calculations yield minimum energy C–O distances similar to those found in carbonates (Table 1.4)^{27,28} although

Table 1.5 Comparison of experimental IP's and SCF-X α and HFR relative orbital energies (eV) for CO $_3^{2-}$

MO	Experimental	SCF-X α	HFR
$\left. \begin{array}{l} 1a_2' \\ 1e'' \\ 4e' \end{array} \right\}$	0	0 -1.6	0
$\left. \begin{array}{l} 3e' \\ 1a_2'' \end{array} \right\}$	-6.0	-5.5	-6.0
4a $_1'$	-7.7	-7.6	-8.0
2e'	-19.8	-18.2	-23.3
3a $_1'$	-24.1	-21.4	-27.7

incorporation of lattice effects to obtain trends from one carbonate to another have proved difficult. Ionization potentials from photoelectron spectra are found to be virtually identical for all carbonates, with the spectrum consisting of O2p non-bonding orbital, C-O bonding orbital and O2s orbital regions as shown in Fig. 1.3.^{29,30} The qualitative features of the spectra have been reproduced by both HFR³¹ and MS-X α ³² cluster calculations, although quantitative discrepancies are substantial (Table 1.5). Such a comparison of calculation and experiment can be only semiquantitative since ionization potentials are not accurately equal to negatives of ground state orbital eigenvalues in either theoretical method, and since the necessary correlation, relaxation and localization corrections to the calculated ionization potentials have not been made. Many body perturbation theory studies have shown, in particular, that inner valence orbital ionizations, such as O2s, may be strongly modified by such effects.³³

Now consider the definition of a cluster for a more difficult case, B $_2$ O $_3$. The simplest cluster, BO $_3^{3-}$ shown in Fig. 1.4, has a large negative charge and can only be formed by breaking strong covalent B-O bonds. As might be expected,

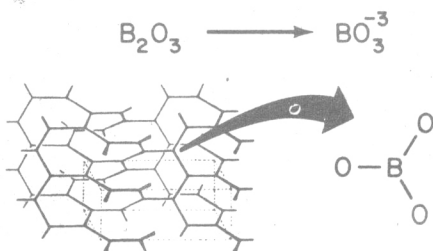


Fig. 1.4 BO $_3^{3-}$ cluster abstracted from B $_2$ O $_3$.