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'PROPERTIES OF THREE-DIMENSIONAL ENERGETIC SOLIDS AND MOLECULAR CRYSTALS"

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This study is a theoretical investigation of the wide range of phenomena exhibited by energetic materials in their solid phase and other prototypic molecular crystals. Very little is known about the electronic structure of this class of materials, and this is especially true under conditions of extreme temperature and pressure. Two complementary ab initio techniques based on the Hartree-Fock model have been undertaken to elucidate the electronic structure: energy band theory which uses the translational invariance of the solid, and finite molecular cluster modeling which probes local phe-

Block 20

nomena. The initial coding for bulk and surface energy band calculations
using the linear combination of molecular orbitals approach has been imple-
mented and tested. Currently the final stages of the calculation are being
debugged. This is made difficult by the complicated rotational properties
of the molecular basis vectors and the lack of a benchwork energy band cal-
culation for molecular solids. Molecular methane has been studied using the
cluster model. Computations employing many body perturbation theory have
been concluded on the ground and excited state including the Jahn-Teller
effect. A bulk solid simulating cluster of thirteen methane molecular units
has been employed to study the ground state properties. The excited state is
presently being explored.

1. Contract Description.

This project is designed to investigate a wide range of phenomena on energetic materials in their solid phase and also on other molecular solids which serve as prototypes to allow calibration of the methods. These studies are all theoretical in nature and are employing non-parameterized _ab initio_ techniques.

In the case of solid fuels or explosives the area of initial relevance is the initiation of the combustion or detonation. This may be by means of a strong shock wave impinging on the material and/or by means of a high temperature. Therefore one of the principal objectives of this research is to study the behavior of simple molecular solids under extreme conditions of pressure and temperature. Using normal techniques of solid state theory studies of elevated pressure are possible, although certain properties of molecular solids substantially complicate this. Normal solid state models are essentially $T = 0$ models for the electronic structure and basic theoretical developments are needed to permit determination of the electronic properties at elevated temperatures. We are to undertake ultimately such developments.

Once initiation of combustion or detonation is achieved one needs to understand how it is sustained. This process may for example be autocatalytic in nature. It seems clear that the region of the sample near the point of initiation will to some extent at least see similar extreme conditions to those seen at the point of initiation. Thus the modifications of the system properties by extremes of pressure and temperature take on substantial importance. Therefore our early efforts are aimed at determining the properties of molecular solids under such conditions. Some ramifications of this are detailed later in part 3.

The ultimate question of stability of the system and its properties may also be determined by impurities and defects. It is intended to determine

what the effect of defects and impurities are on all possible properties of the molecular systems. As is perhaps obvious, studies on the surface and the bulk are needed.

2. Partial List of Unsolved Scientific Problems Related To Molecular Solids.

If one excepts the solid rare gases, and such essentially one dimensional systems as polymers, very few studies of a theoretical nature have been performed on the fundamental electronic structure and related properties of molecular solids. The few studies available become zero in nature when it concerns the fundamental properties of such systems under extremes of temperature and pressure. At the very least, the studies supported by this contract will be a substantial beginning in the determination of such fundamental properties of three dimensional molecular solids as the charge density, the electronic density of states, the optical spectra including excitons, band edges and core level excitations for both bulk and surface at normal pressure and T = 0 and we believe for the extremes of pressure and also temperature. In these latter cases the interaction of vibronic properties and electronic may well be dominant.

The essential nature of the problems here may be quickly illustrated by consideration of the simplest molecular system, the solid rare gases. Here we exclude solid He as a pathological case. The fundamental density of states is understood for Ar, Kr and Xe but not for Ne. The band edges and excitons are basically understood for all these systems. However when abnormal conditions are introduced the major area of understanding reduces to zero. Consider solid Xe. Some investigators find evidence for metallic Xe at a pressure of ~0.3 M bar. Contrarily other groups find Solid Xe at 0.6 M bar still transparent implying a real band gap of 3 eV or more. Theoretically in the close packed fcc phase S. B. Trickey and myself find Xe to metallise at ~1.4 M bar.

We also find that Xe might metallise in a bcc (a non close packed phase!!) at a pressure of 0.7 M bar provided a phase transition to bcc were possible there. Current theoretic results find the free energy for such a transition within the realm of possibility but still uncertain. The entire high pressure properties of Xe is an open book yet.

The case of more usual molecular solids is further removed from understanding. The inherent molecular nature is a complication. Consider a simple non trivial system, solid CH_4. Crystalline CH_4 is a van der Waals solid in which the C's form in a fcc lattice just as do the atoms in solid Xe. The H's are tetrahedrally coordinated about the respective carbons. The H's do not necessarily coordinate their positions from CH_4 unit to CH_4 unit. Theoretically little is known about solid CH_4 other than its possible valence band structure at normal pressure and $T = 0$. A complete band structure, bulk and surface, and excitonic computation are in order here. There is a wealth of reliable experimental data to explain and coordinate with here.

Consider CH_4 under pressure, one needs answer the questions, under what pressure condition does the CH_4 unit maintain its molecular integrity, when does it become a mere collection of C's and H's or metallise? What is the lattice arrangement of the C's in all regions and how do the H's coordinate with the C's? If one can answer all the above geometric questions via total energy studies, then one can construct a band structure and elucidate the fundamental electronic structure of this system as a function of pressure.

Similar considerations apply to solid NO as well except less is known theoretically than for CH_4. This then is an outline of basic questions to be answered. There are others as well as a host of less fundamental but very important technological questions which are also in need of study such as the role of imperfections in all facets of molecular crystal properties.

3. Scientific Approach and Progress in its Implementation.

Two fundamental approaches are to used here. The first which is applicable to bulk and surface properties having translational invariance is energy band theory, the second which is applicable to properties not having translational invariance is finite molecular cluster modeling of an extended system. This latter approach allows us to model the extended system by a cluster of 20 molecules or so (for CH_4 this implies 20 C's and 80 H's or 20 N's and 20 O's for NO etc). This cluster treats all electrons in the cluster and models the environment with an appropriate boundary potential. This basic philosophy has been discussed in "Theory of Chemisorption" ed. J. R. Smith, Springer-Verlag, 1980.

The unifying thread of these complementary approaches is the use of the Hartree-Fock method, in its Unrestricted Form where pertinent, for the initial study in all cases. Extensive experience with Hartree-Fock for solid rare gases, alkali-halides and other solids teaches that such techniques are inadequate and an explicit treatment of correlation is needed. The fact that we are dealing with a solid eliminates many possible approaches due to the problem of size consistency. This problem was most clearly defined by E. Davidson who demonstrated that single and double replacement CI approaches for a dilute He atom gas was in substantial error in predicting total correlation energy. Similar difficulty may be found for higher replacement CI methods as well. Furthermore our studies show that not only is the total correlation energy in error but the changes in it upon excitation or ionization were in error as well. One must, we feel, use a size consistent method. Ideally one would like it to maintain its consistency at each level of approximation. There are several methods which in principle meet these needs. Of these methods we investigated two; the Independent Electron Pair Approximation and Ray-

leigh-Schroedinger based Many Body Perturbation Theory. These were chosen due to their being practical now for such studies whereas methods such as coupled cluster or generator coordinate models need much development to be practical for such studies. Both IEPA and MBPT have been coded and tested. The essential conclusion is that the MBPT method will be used for future development. A discussion of the problems in implementing this will be given later.

In order to implement the Hartru-Fock energy band method for molecular solids, several modifications in traditional energy band theory were desired. Most modern energy band calculations which do not employ empirical potentials or severe potential approximations are based upon the LCAO method, (Linear Combination of Atomic Orbitals). Since questions relating to properties under extreme conditions are to be answered, self-consistency is essential. Consider now the canonical LCAO method as it applies to a minimally accurate computation for CH_4. Use a double zeta set here. This requires 2 s orbitals/H, 4 s orbitals/C and 3 x 2 p orbitals/C for a total of 18 orbitals. At this level CH_4 molecule is badly described in terms of its bonding properties. Bond polarization orbitals are needed as well. One can place p, d, f like function on C and/or H or use bond centered functions. We find this latter most effective and one needs at least 1 s bond orbital/bond or 4 in CH_4. Thus in the least sizeable LCAO option one needs 22 orbitals for CH_4. This set doesn't describe the virtual states well. The basic integral problem goes as N^4 and is unaltered by any further manipulation. However the SCF times go as N^3 and can be reduced. This is very important because in a given run the integrals are only computed once. Due to Bloch symmetry in a single SCF cycle one diagonalizes the Fock operator for a mesh in reciprocal space of order 100 points. This is repeated until convergence, say 10 times so that the N^3 part is done 10^3 times in a single computation. Thus this part is the true time limit here. A simple change of procedure

eliminates the problem. Instead of using an LCAO basis contract the AO's including bond polarization functions into molecular orbitals (MO's). Doing this in double zeta at $\underline{no}$ loss in accuracy for CH_4 reduces the basis set from 22 to 10. Thus the N^3 part is speeded up by a factor of 10. For larger molecules the factor is even greater. Furthermore the basis vectors here inherently have the proper symmetry of the unit cell. Unfortunately current developments haven't implemented this possibility. We have therefore undertaken the construction of the appropriate code based upon a contracted gaussian basis set. All needed codes have been written by us. The method is straight foreward. A labels generation is done. The determination of the needed labels is greatly facilitated using the translational symmetry of the solid (need be only 1 dimensional) and by the use of symmetry MO's for the basis set. An integrals run is made next using the labels generated earlier and a basis set of contracted GTO's. In a given contraction a GTO may have any origin and as many different origins as GTO's are allowed in a single contraction. Furthermore within the confines of an s, p, d basis set each gaussian in a contraction may have a different symmetry type. This is a marked extension beyond packaged codes. This is necessary to implement the SCF-LCMO idea. The labels generator and integral codes are tested and working. After this point a straight foreward implementation of a band theoretic SCF cycle is introduced. This latter is not trivial to envoke however due to the need to work on a mesh in reciprocal space and due to complicated rotational properties of the basis vectors. The appropriate coding has been written and is being debugged now. The debugging is tedious due to lack of benchwork crystal calculation for molecular solids. It is risky to predict here, but we believe this will be complete in about 60 days ± 30. Speed is quite high in this code and flexibility great so that detailed studies will be rapidly completed upon final debug.

The essential features of the new approach have been simulated for simple systems, the alkali-halides and silver-halides, for which we know some of the answers using existing software. These tests were fully successful and produced results of interest. These results are being sent to Physical Review for possible publication.

The second area of needed development is in the implementation of MBPT for cluster or band calculations. The initial phase of this is complete and tested and used for prototype studies including CH_4. The practical aspects of this were considered in our progress report submitted about February 1 and need not be repeated here. The essential limitation on this application is the rotation from basis vectors to Fock vectors which goes as N^8. This is largely overcome by a quad linear scheme which reduces the problem to N^5, still formidable. The N^5 rotation is in "vector" form however and can be reduced to N^4 by an array processor. The University of Illinois MRL has made one available to us on a 1/2 time basis at no cost. Using this a maximal calculation on a cluster of 20 CH_4's can be accomplished in about 10 hours, an acceptable cost in time on a small computer. In addition, Michigan Technological University continues to support this project by providing additional VAX hardware for this project. The support of both universities is substantial and essential.

Using MBPT computation on ground and excited CH_4 are finished including Jahn-Teller effect. A bulk simulating cluster of 13 CH_4's is complete for the ground but not excited state. A computation using 9 CH_4's simulating a (100) surface is to follow. The adsorption of O_2 onto this surface will then be studied along with how pressure and imperfection modify such. This study should be complete by 1 January 1983. Similar studies on solid NO will be initiated by this summer at the latest.

4. Publications.

Two manuscripts submitted to Physical Review:

1. A Study of the Electronic Structure of Twelve Alkali-Halide Crystals, A. B. Kunz.

2. The Electronic Structure of AgF, AgCl and AgBr, A. B. Kunz.

Several other manuscripts are in preparation on the results of the various initial results and tests including the CH_4 study.

5. There will be no unspent contract funds this year.

6. Other Support of the Principal Investigator.

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