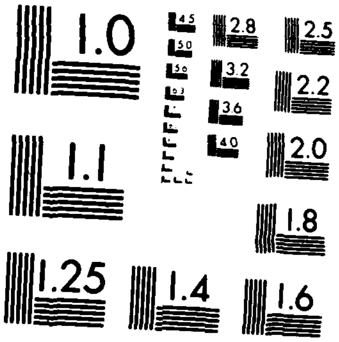
AD-A128 735 PROPERTIES OF THREE DIMENSIONAL ENERGETIC SOLIDS AND MOLECULAR CRYSTALS(U) MICHIGAN TECHNOLOGICAL UNIV HOUGHTON A B KUNZ 01 JUN 83 N00014-81-K-0620 1/1

UNCLASSIFIED F/G 21/2 NL



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AD A128735

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(12)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
2. GOVT ACCESSION NO. AD-A128735
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) Properties of Three Dimensional Energetic Solids and Molecular Crystals

5. TYPE OF REPORT & PERIOD COVERED 2nd Annual Technical Report 1 July 1982- 1 June 1983

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
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8. CONTRACT OR GRANT NUMBER(s) ONR-N-00014-81-K-0620

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Michigan Technological University
Houghton,Mi. 49931

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Arlington,Va. 22217

12. REPORT DATE 1 June 1983

13. NUMBER OF PAGES 8

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report) Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release:distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

DTIC
ELECTE
MAY 31 1983
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Energetic solids,solid fuels,molecular crystals,combustion,excitons, energy bands,ab initio theory, methane, nitric oxide

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

The effect of exciton formation upon combustion of solid fuels is examined by applying ab initio theory to solid methane and nitric oxide

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

TECHNICAL REPORT ON GRANT ONR-N-00014-81-K-0620

PERIOD 1 JULY 1982 - 1 JUNE 1983

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

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1. Contract Description.

The focus of this project remains to investigate a wide range of phenomena relating to energetic materials in the solid phase. In addition it is proving necessary to extend the range of applicability of existing techniques and to develop new methodology to enable sufficiently accurate studies at an atomistic level on these little studied systems (this is so at least in the level of traditional solid state physics methodology). The need to develop new methods also necessitates a few simple studies on prototype systems for which competing theoretical calculations are available and also for which definitive experimental data may be available. All theoretical studies undertaken or proposed are to be of the _ab initio_ type.

In the case of solid fuels or explosives the area of initial relevance is the initiation of the combustion or detonation. In the real world this may be by means of a strong shock wave impinging on the system and/or by means of elevated temperatures. At an atomistic level this means one looks for methods to lessen the energy required to produce structural/chemical modifications and the means by which energy is transported to such sites. In practice we shall see that such modifications are caused/accompanied by localization of energetically excited states. Such localization may occur either at defects or impurities or may spontaneously occur when an 'exciton' causes sufficient distortion of the local lattice so as to localize in space its energy. A complication of this study is that the interesting behavior occurs under conditions of extreme temperature or pressure. Most traditional solid state or quantum chemical approaches to electronic structure determination are T=0 type theories even when elevated pressures are considered.

After combustion is initiated it is essential to understand how it is sustained as well as how it is quenched. The process of sustaining combustion may well be autocatalytic in nature. It seems clear that the portions of the sample near the point of combustion will see to some extent at least the same extreme conditions as during initiation. The modification of the system by such extreme conditions therefore takes on great importance, and our early efforts have been directed along such lines.

The ultimate issue of stability may well be determined by impurities or defects. It is proposed to determine what the effect of defects and impurities are on all possible properties of these molecular systems that may relate to combustion/detonation. It is clear that studies on both surfaces and bulk systems are essential.

2. Short List of Unsolved Scientific Questions Related to Molecular Solids.

If one excepts the solid rare gasses and to a lesser extent solid CH_4, and such essentially one dimensional systems as the various polymers, few if any atomistic theoretical studies have been successfully performed for molecular solids. The few available studies ignore, other than for several solid rare gasses, systems under extremes of temperature or pressure. At the very least, the studies supported by this contract are to provide 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 size and nature of the fundamental electronic excitations and possibly atomic distortions of the basic unit cell upon electronic excitation or under exposure to elevated pressure.

In order to fully appreciate the difficulties consider the case of solid CH_4, the best understood solid of this type. Crystalline CH_4 is a van der Waals solid in which the carbon atoms form in a close packed fcc lattice. The H's however form in tetrahedral symmetry about each C atom but do not achieve any long range order. Thus in the ground state the basic CH_4 unit is free to rotate and in many respects behaves as a spherical molecule. Does this simple behavior extend to the excited configurations as well?

It is clear that little definitive is known about solid CH_4, and it must be conceded that even less is known about a more interesting system, solid NO. Nonetheless, from what is known it is quite clear that there are definitely peculiar properties associated with the geometry and electronic structure of this solid. The crystallographic unit is $(NO)_4$. This unit does not appear to have a strong chemical identity however, but rather is composed of two N_2O_2 units. The evidence for this is the following: the separation of the two N_2O_2 units is large and the magnetic properties of the unit $(NO)_4$ are similar to the N_2O_2 unit, being diamagnetic. This is in some ways puzzling in that within a N_2O_2 unit the separation of the two NO molecules is far greater than in free space, making strong interactions of the two units unlikely. Furthermore, the individual NO molecule is known to be paramagnetic. The fact that the individual N_2O_2 unit is diamagnetic indicates some real interaction between the two NO units must exist despite the large separation. This all raises important questions regarding solid NO. What is the nature of the fundamental electronic excitations of the solid form and how do they relate to those in the free NO molecule? Is the basic unit able to maintain its geometry under pressure and if not then what modifications occur, and at what type of pressure?

3. Scientific Approach and Recent Progress in its Implementation.

Two complementary approaches are to be used: the first of which is applicable to bulk systems and to ordered surfaces. This is traditional energy band theory. In its current implementation, we employ the Linear Combination of Molecular Orbitals method (LCMO) in a self consistent Hartree-Fock (SCFHF) approach. This level of theory is augmented by a direct application of (nearly) degenerate perturbation theory including corrections to the second order, to enable us to include relaxation corrections, correlation corrections and the formation of localized electron-hole pair excited states (excitons). Extensive calculations of this type have been performed for solid CH_4 and the results prepared for publication. As a substantial detailed manuscript for this exists, I shall not repeat the lessons learned in this report.

The second approach is to model systems by finite cluster techniques. These methods are of particular importance for phenomena in which substantial departure from translational invariance are expected. This would definitely include the case of lattice distortion accompaning an excitation or around a defect or impurity. In the implementation of the finite cluster method, we treat all electrons and nuclei inside the cluster in an Unrestricted-Hartree-Fock (UHF) way and augment the UHF results in all cases with a perturbative calculation of the correlation properties. In the case of near degeneracies we also perform a nearly degenerate perturbation treatment as well. This is of value in that by such means we eliminate the broken symmetries of the UHF method and recover Multiplet Structure. In all cases we solve for the basic UHF state in a self consistent manner, and thus spectral detail is obtained by taking differences of total energy,rather than from some more approximate way.

Substantial effort has gone into determining the accuracy needed in perturbative treatments in order to predict spectra. Dr. Beck has for example studied first the Methane molecule. Using an enlarged basis set including f-orbitals, he has succeeded in obtaining 90% of the total correlation energy in both ground and excited state. In doing this one computes to high accuracy and great expense the correlaton energies of the cores and other levels not involved in the electronic transition. These correlation contributions largely cancel upon electronic excitation except for those few terms associated with the ruptured bonds. We have studied the use of smaller correlation bases, which primarily describe the electrons which participate most in the excitation. Our MBPT code was organized to produce intermediate output which facilitated our being able to determine this answer. A test of the restricted basis was made. The total correlation energy is only about 50% of the experimental value, but the change in total energy upon excitation is essentially unchanged. This technique is extended to solid CH_4. In the case of a bulk cluster we use 13 CH_4 units for a net of 65 atoms. All electrons are treated here. The excitation energy is computed and reexamined upon distortion of the base Methane unit. The fundamental exciton is stable against ionization by an amount greater than 1 eV. and a D_{2h} distortion is further stabalized by in excess of 1.5 eV. This is consistent with the earlier energy band theory results as well.

A second cluster of 9 methane molecules was treated to simulate a surface situation. Again the simple exciton in the ideal T_d geometry was found to be stable against ionization, and had an excitation energy close in value to the free molecule. Distortions in response to this excitation may be in either a C_{2v} or a D_{2h} mode. Both are considered. The lowest excited state appears to have a C_{2v} geometry in which the elongated H_2 bond lies into the solid. This is relevant in the extreme to the present study. The presence of an electrical excitation at the surface of solid Methane causes an exciton which spontaneously lowers the symmetry of the system and partially predissociates the excited CH_4 molecule into a CH_2 unit and an H_2 unit. Both these units are inherently reactive. A report of these studies should soon be prepared for publication.

5. Publications and Related Documentation.

1. A.B.Kunz,Study of the electronic structure of twelve alkali halide crystals, Phys. Rev. B 26,2056-2069(1982).

2. A.B.Kunz.Electronic structure of AgF,AgCl,and AgBr,Phys. Rev. B 26,2070-2075,(1982).

3. Several manuscripts submitted for publication or in preparation.

4. A.B.Kunz will present a series of lectures derived from this research at a NATO advanced study institute in Braunlage-Harz this August.

5. A.B.Kunz will present an invited lecture on results partially supported by this grant and partially by the NSF at the October Meeting of the American Society For Metals and the Metalurgical Society.

5. No current contract funds will be unspent by 1 July 1983.

6. Other Support for the Principal Investigator.

A.B.Kunz receives support from the National Science Foundation through thr MRL program Grant NSF-DMR-80-20250 at a current annual level of $130000.

7. Other Support

D.R.Beck and R.S.Weidman received an equipment grant in the ammount of $25000 from the National Science Foundation.