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Progress Report on Grant ONR-N-00014-81-K-0620

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

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Dr. Bobby Junker
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Dear Bobby,

Enclosed is a brief progress report for our initial 6 months effort. In about 3 months a more comprehensive report to introduce our second year's effort will be forthcoming. I have your questionaire for this purpose. Things seem to be going well and this multi university effort seems to be a reasonable way to live. Best wishes.

Sincerely yours,

A. Barry Kunz

ABK:mpb

Enclosure

Period Covered: 1 July 1981 to 31 December 1981.

Definition of the Initial Problem.

This is the initial six months of this project. The ultimate goal is to provide a comprehensive atomistic level understanding of rapid combustion or explosion of solid phase energetic materials. This understanding is to include ultimately the question of initiation of the rapid oxidation, the sustaining of the rapid oxidation and its ultimate quenching. In addition atomistic factors related to stability, ageing and reliability are to be investigated. In order to facilitate this initial phase of the study prototype materials have been selected for study. These prototypes are CH_4 and and NO. The initial progress has been of two types. Specific results for the CH_4 system and development of condensed matter physics techniques in ways optimally appropriate for molecular solids. The initial choice of CH_4 was based upon two factors. The first and dominant factor is the availability of excellent data on the structure and electronic spectra of CH_4 in both gas and condensed phases. The second factor is that both gas and condensed phases of CH_4 have high symmetry of simple types. The CH_4 ground state in molecular form is T_D and the most interesting low lying excited states are either T_D or D_{2h}. In condensed form the CH_4 molecules are in a fcc array (symmetry O_h). The initial studies on CH_4 are attempts to characterize the ground and low lying excited states of CH_4 in vacuum, bulk solid and at a solid surface. This knowledge is of twofold importance. Firstly we are discovering what properties of CH_4 result from its molecular nature as opposed to those properties which are specifically a result of the condensed phase or which are due to the presence of a surface. The second lesson to be learned is what degree of accuracy must be maintained in the

models and calculations in order to distinguish among these effects.

Progress to Date.

Initial results have been obtained for the methane molecule in both ground and low lying excited states. These calculations were necessary for two reasons. The first was to develop accurate gaussian basis sets to be used later in solid state calculations. The second reason is to provide gas phase predictions of sufficient accuracy so that later solid and surface results could be analyzed to permit the identification of surface and solid phenomena as distinct from molecular phenomena. The results were obtained using two basic approaches. The first is restricted Hartree-Fock (self consistent for each state in question) plus Configuration Interaction employing single and double excitations. This is performed using program MOCI written by D. R. Beck. The second method is based on the unrestricted Hartree-Fock approximation (self consistent for each state in question) plus many body perturbation theory. This is performed using program MBPT written by A. B. Kunz. The results of the two methods are in full accord to the level of 0.1 eV or so. Results may be summarized as follows. The ideal T_D geometry is used first. The HF ground state energy is found to be -1093.57 eV. Correlation among only valence levels lowers this by 3.61 eV. The first ionization potential is found to be 13.66 eV in the HF limit or 14.10 eV in the correlated case. Experiment is 14.39 eV. The carbon K shell IP is computed to be 290.45 eV versus an experimental value of $290.6 \pm .1$ eV. In the case of excitation to bound excited states, the lowest lying excitation is to a triplet state. The HF prediction is 9.93 eV and the correlated prediction is 10.21 eV. This is found in gross disagreement with a putative experimental identification of 8.9 eV. We believe the experimental identification is in error as outlined later. The lowest

singlet excitation lies 0.5 eV above the triplet and agrees well with an experimental value of 10.8 eV.

The ground state of CH_4 is a singlet state and hence the singlet-triplet excitation is difficult to identify unambiguously. We have investigated alternate geometries for the excited states. The triplet state is found to minimize in a D_{2h} geometry, along with a 1.5 eV lowering. Thus the triplet state lowers to an excitation energy of 8.7 eV. We believe the weak edge identified experimentally is in fact a non Franck-Condon principle excitation from a T_D to a D_{2h} geometry. Basically we consider these initial molecular studies satisfactory.

Initial attempts at considering solid methane are based upon the R.H.F. + C.I. model in a large cluster approximation. The cluster consists of a central CH_4 plus its 12 nearest neighboring CH_4's. Thus the cluster has 65 atoms in it. Currently the ground state of this cluster has been computed. Calculations are in progress to determine the first I.P. and the low lying electronic excitations. It will be of particular interest to see if molecular distortion upon excitation will be as significant in solid as for gas phase.

Finally significant progress has been made in basically solid state approaches to the molecular problem. This consists of formulating and coding a UHF approach to the traditional energy band problem in a way both efficient and amenable to inclusion of correlation corrections via the MBPT route. The need for this development may easily be seen. Consider a simple double zeta approach to solid methane. The solid crystalizes in an O_h (fcc) structure with only one CH_4 per cell. In any traditional approach one places basis functions independently on each atom in a cell. For CH_4 this is 2 s orbitals per H (double zeta), 4 s orbitals for C and 6 p's as well for a total

of 18 orbitals in a simple double zeta set. This is not adequate even for gaseous CH_4 as bond functions are needed as well. The simplest adequate form are a pair of s functions centered on each bond center. This augments the basis to 26 functions for the CH_4 solid ground state. As unit cells get more complex this number expands unreasonably. The simple solution is to reformulate the problem in terms of MO's not AO. Here a double zeta set with bond functions and all is just 10 functions of a more complex nature. Existing codes are not suited to this and new codes have been generated. These are in the test stage. The formulation details will be reported later after debugging of all new codes is complete as some of the ideas will be of value to people doing large molecule ab initio computations. Preliminary studies on some traditional solids to test these ideas have been completed.

Future Directions.

The immediate future is well defined by the extent of progress to date. We shall complete the bulk methane large cluster study. Upon this completion a similar study will be made upon a cluster modified to represent the methane surface. This study should be complete in the next 6 months. After completion of the surface study, studies of the molecular destruction at the surface will begin. This will include studies of detachment of CH_4 groups as well as H or H_2 from a CH_4 and the response of this surface to O or O_2. These studies will have obvious relevance to combustion and explosion. As these studies progress we will simultaneously begin studies of like nature on NO.

The solid state approaches shall be tested and CH_4 results obtained by the end of the next 6 month period. Studies of how CH_4 properties are affected by pressure, hydrostatic or uniaxial will then commence. We thus expect to have comprehensive ideas of the gas, solid and surface properties of CH_4 and response to O, O_2 and extreme pressure completed in the next 18

months. Collateral studies on NO using the solid state techniques will be commenced as progress on CH_4 warrants.


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