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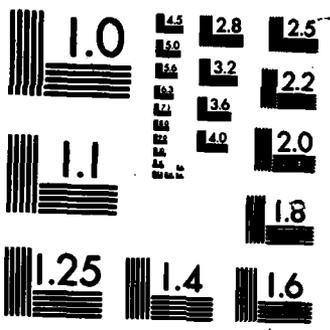
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Energy Trapping, Release, and Transport in Three-Dimensional Energetic Solids and Molecular Crystals.		5. TYPE OF REPORT & PERIOD COVERED 4th Annual Technical Report 1 January 1984-31 December 84
7. AUTHOR(s) A. Barry Kunz Department of Physics		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Michigan Technological University Houghton, MI 49931		8. CONTRACT OR GRANT NUMBER(s) ONR-N-00014-81-K-0620
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE
		13. NUMBER OF PAGES
		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 Cont'd		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Energetic Solids, molecular solids, clusters, defects, impurities, ICECAP.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In this report we describe progress in developing and implementing a general theoretical approach to describing the properties of defects and impurities of a general nature in non-metallic solid systems. This approach combines fully correlated, fully self-consistent electronic structure determination of the electrical and mechanical properties associated with neutral or charged defects/impurities in or on a non-metal. The system remote from the defect is described by the shell model which incorporates self-consistently, host polarization and distortion. This results in our		

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Annual Technical Report on Grant
DNR-N-00014-81-K-0620
For the period 1 January 1984-31 December 1984

"Energy Trapping, Release and Transport in
Three Dimensional Energetic Solids and
Molecular Crystals: Theory of Defects
and Impurities"

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Abstract

In this report we describe progress in developing and implementing a general theoretical approach to describing the properties of defects and impurities of a general nature in non-metallic solid systems. This approach combines fully correlated, fully self-consistent electronic structure determination of the electrical and mechanical properties associated with neutral or charged defects/impurities in or on a non-metal. The system remote from the defect is described by the shell model which incorporates self-consistently, host polarization and distortion. This results in our being able to obtain absolute energies of the impurity ions in the host and their interaction. The model is free of adjustable or undefined parameters. This project is of non-trivial magnitude and the current computer implementation, which is functional in our laboratory, consists of a program, ICECAP, which is about 100,000 statements long. This program is the result of extensive collaboration between our group and that of Professor J. M. Vail, University of Manitoba, and of Dr. A. M. Stoneham, Harwell, AERE.

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Absolute Energies of Impurity Ions and
Defects in Non-metals and their Excitation
Energies and Ionization Potentials

Introduction

The aim of this research line is to obtain absolute energies of impurity ions or defects, including charged states, in non-metals. In addition, the absolute excitation energies of low lying excited states are studied. These calculations will not simply be of one-electron energies, nor will spectroscopy be obtained by using Koopmans' theorem, but rather by evaluation of total system energies and their differences. These calculations will include electron correlation corrections and multiplet splittings. Due to using differences in total energy to generate spectroscopic information, coulomb-hole attractions will be included directly and not as a perturbation.

Such studies are important in a wide range of applications, such as i) spectroscopic and laser applications, where it is necessary to know about the stability of a promising charge state of a particular impurity in a novel host, ii) solid-state reactions, where gas sensors and oxide reactions serve as examples, in which the impurity acts as a source or sink for electrons, exchanging carriers with other species at the surface or in the bulk, and iii) stability of charged imperfections in or on unstable solids (energetic solids), where local deviations from periodicity may control stability of entire systems, iv) etc.

It is clear that these examples show only a small fraction of

the variety of important properties which depend crucially upon the absolute energy. We observe that calculations of the sort described lead naturally to prediction of a wide variety of related quantities. Charge-state stability, for example, is one aspect of the prediction of photoionization energies, but also can lead to the identification of which of several alternate sites in a complex substance is the stable one, to the identification of charge-compensation mechanisms, and to the prediction of limiting solubilities with greater accuracy than current crude charge and size misfit models.

A second key output of such studies can be the development of interatomic potentials, which have a sound theoretical basis, using the best available current technique. These calculations must therefore include electron correlation explicitly. This aspect shall emphasize those cases for which empirical potentials are problematic. These systems include systems as O^{2-} , S^{2-} , Se^{2-} , Te^{2-} , etc. In these cases the free double negative ion is not stable in free space but is only stabilized by its environment. The ionic polarizability of these entities is highly dependent upon the host and perhaps even the local site occupied in the host.

A second category includes systems for which empirical forms are not available. This may be because the species do not occur at the proper separation in well-documented perfect crystals, or because special species are involved, such as $F^- - F_2^-$ or $I^- - O^{2-}$, or because unusual cation - cation interactions occur. The last case is problematic since cations are rarely found close enough to each other to yield more than a very small component of the total

energy of perfect crystals.

A third category includes a wide variety of other cases which include systems in unusual charge states such as Fe^{2+} in SrTiO_3 or Fe^+ in MgO . Impurity systems in their excited states are also included here, which are not included in traditional approaches.

Any interatomic potentials developed by this project are subject to verification in three ways. These include: i) checks that these potentials provide good values in applications to defect properties (thermodynamic vibrational, lattice expansion, etc.) parallel to similar studies produced previously, ii) checks of predictions over a range of crystals for properties of wider interest, such as electro optic constants in complex oxides, to see if trends are accurately reproduced, iii) checks of transferability for species such as O^{2-} and Mg^{2+} to see to what extent their interatomic potentials are the same in MgO and in complex oxides such as BMAG ($\text{Ba}_2 \text{Mg Ge}_2 \text{O}_7$) or in the bulk and near a surface. This latter study is particularly interesting for the double negative ions in that they are not stable in free space.

These studies are directly applicable to a wide variety of energetic solids including (but not limited to) CH_4 , $(\text{NO})_2$, Nitromethane, RDX.

Methodology

It is of practical importance to be able to calculate reliably properties of defects in crystalline materials. This work relates to methods developed for point defects in ionic crystals, for which many successful ground state calculations have been performed on the basis of a classical, discrete-ion model:

specifically, using the Harwell HADES [1] or related programs. The classical lattice model is inadequate for electronic properties of defects, arising from excess electrons, holes, or impurities, or from strong perturbation of the electronic structure of the host ions by the defect. In such cases, quantum-mechanical treatment of electrons in the vicinity of the defect/excitation is undertaken by considering the defect to be a molecular cluster, embedded in a weakly perturbed classical lattice. In such an approach, three principal questions arise: a) What boundary conditions are appropriate between quantum and classical regions? b) Are the quantum and classical representations of interionic forces compatible? and c) To what extent are existing computational methods adequate to the demands of the approach we envisage? We report progress on the first and third questions and describe how to approach the second.

In the following we describe our physical model including cluster-lattice boundary conditions, a general computer program for such cluster calculations, results of preliminary calculations, and classical representations.

We define the defect cluster as any excess electrons, and/or those ions/atoms that are significantly perturbed by the defect, and or regions in which local excitations occur including both perturbations of their electronic structure and displacements of their nuclei. In this work we usually refer to ions but in our context the neutral atom, or even an entire molecule would be equivalent. The surrounding infinite lattice is a perturbed shell-model crystal [2], in which the ions are represented as

dipole polarizable point charges. Each ion is represented as a point-charge core coupled harmonically (force constant K) to a uniformly charged (charge Y) massless spherical shell of indeterminate radius, and ions interact through Coulomb and short-range shell-model potentials, $v(r)$. The latter are exemplified by the Buckingham form:

$$v(r) = B \exp(-r/p) - (C/r^6). \quad (1)$$

The use of this form is not essential.

In the defect cluster, excess electrons are treated quantum-mechanically, usually incorporated with the electrons of some near neighbour ions. In our work, the electrons of the cluster are treated in the unrestricted Hartree-Fock (UHF) self-consistent field (SCF) approximation [3], based on linear combination of atomic orbital (LCAO) molecular orbitals (MO) corrected for correlative effects by use of Many Body Perturbation Theory (MBPT). In most non metals, the electronic structure of the ions/atoms/molecules is assumed to be well-localized about the nuclei. However, this will not automatically follow for doubly negative ions on the outer boundary of a UHF-SCF region unless the spatial range of the basis AOs is restricted: the Coulomb field of the surrounding point-charge shell-model lattice does not impose localization upon the quantum-mechanical region. This difficulty is currently overcome by associating completely frozen shell ions or by complete-ion pseudopotentials with ions that surround the UHF-SCF region, retaining their classical dipole moments and shell-core interaction energies. A UHF-SCF program [4] which can incorporate such pseudopotentials (as complete-ions

or as ion cores) is applied in this work. More recent theoretical developments, not yet implemented in computer code, solve the boundary layer problem in a quantum mechanically exact way as detailed at the end of this section.

The defect cluster embedded in a shell-model lattice is described mathematically in terms of lattice (ionic shell and core) coordinates, collectively denoted \underline{R} , referred to as the lattice configuration, linear coefficients in the LCAO-MO formulation of the UHF-SCF approximation, collectively denoted $\underline{\zeta}$, referred to as the electronic configuration, nuclear coordinates (nuclear, pseudopotential, and shell-model) in the defect cluster, collectively denoted \underline{R}_c , referred to as the cluster configuration and coefficient A , of excited determinants found by MBPT. (The cluster, and therefore \underline{R}_c , may include shell-model ions whose positions are anharmonically perturbed by the defect). The total energy of the defect $E(\underline{R}_c, \underline{\zeta}, \underline{R})$ is minimized with respect to $\underline{R}_c, \underline{\zeta}$, and \underline{R} :

$$\frac{\delta E}{\delta \underline{R}_c} = \frac{\delta E}{\delta \underline{\zeta}} = \frac{\delta E}{\delta \underline{R}} = 0,$$

(2)

yielding a variational estimate of cluster (\underline{R}_c), electronic ($\underline{\zeta}$), and lattice (\underline{R}) configurations, and of total energy E and the electronic wave function $\psi(\underline{\zeta})$.

These two approaches are merged in such a way that in practice, the excess electrons and UHF and pseudopotential ions are first simulated by fixed point charges, from which HADES determines the polarized, distorted lattice configuration \underline{R} , and the total energy E of the shell-model lattice. The shell-model point charges of the Lattice (\underline{R}), along with the nuclei and pseudopotentials of a fixed cluster configuration \underline{R}_c , are now applied as a background potential for the UHF-SCF solution

ξ , yielding total electronic energy E_A and wave function $\psi(\xi)$. Ideally, the point-charge simulation of the cluster in the HADES calculation should have all its electric multipole moments identical to those of the UHF-SCF cluster, but this is obviously not practical. One therefore matches only a finite set of low-order multipoles. This is accomplished by introducing additional point-charge simulators into the HADES calculation, representing a small dipole, quadrupole, octupole, etc., correcting for the discrepancies between HADES and UHF-SCF up to a given multipole order, and then iterating the HADES/UHF-SCF up to a given consistency. This procedure is repeated for each increment δR_C the cluster configuration, until minimum total energy E is obtained. This energy is:

$$E = (E_H - E'_C - E'_S) + (E_A + (E_A + E_C + E_D)), \quad (3)$$

where E_H and E_A are defined above, E'_C and E'_S are the shell-model Coulomb and short-range interactions of the cluster region in the HADES calculation that will be replaced in the UHF-SCF calculation by electronic Coulomb and short-range interactions in E_A and by nuclear and pseudopotential Coulomb interactions E_C , and E_D corrects for the energy of the dipoles from the HADES calculation that become associated with complete-ion pseudopotentials.

In preliminary work, the Lattice R includes only ions out to a distance beyond which the defect cluster's electric monopole moment (total charge) dominates, where HADES uses continuum theory to determine the discrete-lattice polarization. Since the potential of such a polarized continuum would be constant within the cluster, as assumed in our calculation, there is a small discrepancy because the medium is in fact discrete. This will be

eliminated as time permits.

The UHF-SCF program [4] used in our work has available a many-body perturbation theory correlation correction [5]. Because UHF-SCF calculations become very time-consuming as the number of electrons rises above 200, the cluster size is somewhat restricted, and correlation correction, which is additionally time-consuming, cannot be applied with abandon. Presently, clusters of more than a few lattice spacings in radius cannot be analysed in this way, and therefore diffuse electronic states of localized defects [6] are not accessible.

The physical model described above has a quantum-mechanical defect region (UHF-SCF with pseudopotentials and correlation correction), with perfect lattice boundary conditions (complete pseudopotentials with dipole correction), embedded in a classical lattice (shell-model), solved variationally by energy minimization with respect to cluster, electronic, and lattice configurations, to finite-order multipole consistency. [Fig. 1]

The computer program is based on HADES [1] and UHF [4] programs, both of which have been extensively tested, refined, and applied. Consequently any point defect configuration in any ionic crystal host lattice geometry can be analysed, provided shell-model parameters and adequate computer time are available. Atomic orbital sets may include s, p, d, and f types (except that the pseudopotential option cannot accept f-type orbitals yet). Either norm-conserving BHS [7] or Phillips-Kleinman [8] pseudopotentials can be used, and correlation corrections can be included in the energy. Octupole consistency is presently available. The program

is currently operating on the Harwell IBM 3081 computer, and the VAX-FPS system at Michigan Technological University.

The dominant computer time bottleneck is in the UHF-SCF process and in application of MBPT. We consider now some computer dependent ramifications of this and indicate approaches to solution.

In all our studies the Unrestricted Hartree Fock (UHF) method is employed as a starting point, as is the normal non-relativistic Hamiltonian. It is assumed the nuclei are infinitely massive and the Born-Oppenheimer approximation is used. Ideally, one would like to solve the n-electron Schrodinger equation. However, exact solutions to (2) are seen as impractical for these systems, and we resort to the UHF approximation. That is, one approximates the solution by a single Slater determinant of one electron orbitals, ϕ_i^α . In the UHF approximation, these orbitals are constrained to form an orthonormal set and to be eigenstates of the z component of spin. The orbitals are not constrained to be double occupied or to have well defined symmetry properties. Choosing the orbitals variationally yields the Hartree-Fock equation:

$$F(\rho^\alpha) \phi_i^\alpha = \epsilon_i^\alpha \phi_i^\alpha, \quad (4)$$

where

$$\rho^\alpha(\vec{x}, \vec{x}') = \sum_{i=1}^n \phi_i^\alpha(\vec{x}) \phi_i^\alpha(\vec{x}'), \quad (5)$$

and

$$F(\rho^\alpha) = -\frac{\hbar^2}{2m} \nabla^2 - \sum_I \frac{e^2 Z_I}{|\vec{r} - \vec{R}_I|} + e^2 \int \frac{\rho^\alpha(\vec{x}', \vec{x}')}{|\vec{r} - \vec{r}'|} - e^2 \int \rho^\alpha(\vec{x}, \vec{x}') / |\vec{r} - \vec{r}'| P(\vec{x}, \vec{x}').$$

(6)

$P(\vec{x}', \vec{x})$ is the operator which replaces coordinate x with x' .

For a solid system with low symmetry, such as a solid with a point defect, solutions to even the UHF system of equations are expensive to encompass. It is useful to make use of the arbitrariness of the Fock equation and to rotate to local solutions if possible. The way this is done has been given by Kunz and Klein [3] and further developed by Kunz [5]. This technique is most useful for non-metallic systems such as are studied here. One formally partitions the system into two parts, the cluster to be studied and its environment, which is found using the HADES method. The cluster is solved self-consistently in the field of the environment.

The UHF method omits correlation effects. A brief description of the methods being currently employed is in order. Correlation methods to be used for extended systems are constrained by size consistency considerations [9,10]. Our group has chosen to use those based upon multi-reference many body perturbation theory (MR-MBPT). Let the exact Hamiltonian be partitioned into a "simple Hamiltonian," H_0 , chosen to be the sum of the one-body Fock operators for the n-body system. Thus

$$H = H_0 + V$$

(7)

and

$$H_0 \phi_i = w_i \phi_i.$$

Consider the first n eigenstate of H_0 separately. There may be no state of H_0 degenerate with these n -states unless it is also included in the n . P is a projector onto the space of these n states and is,

$$P = \sum_{i=1}^n |\phi_i\rangle\langle\phi_i|.$$

Consider,

$$H \psi = E \psi = (H_0 + V) \psi$$

assume we wish to find state ψ , say. Then

$$H_0 \psi = (E - V) \psi \text{ and}$$

$$(1 - P) (H_0 - w_1) \psi = (1 - P) (E - w_1 - V) \psi.$$

Commuting $(1 - P)$ with $(H_0 - w_1)$ permits one to obtain the formal solution for ψ

$$P\psi = \psi - (H_0 - w_1)^{-1} (1 - P) (E - w_1 - V) \psi.$$

Now

$$P\psi = \sum_{j=1}^n \phi_j \langle\phi_j|\psi\rangle = \sum_{j=1}^n \pi_j \phi_j = \phi.$$

ϕ is of course unknown. Nevertheless one finds

$$\psi = T\phi,$$

(8)

where

$$T = \{ 1 - (H_0 - w_1)^{-1} (1-P) (E - w_1 - V) \}^{-1}. \quad (9)$$

One may obtain the energy from the secular equation:

$$(E - w_1) \pi_i = \sum_{k=1}^n \pi_k \bar{v}_{ik}, \quad (10)$$

where

$$v_{ij} = \langle \phi_i | VT | \phi_j \rangle \quad (11)$$

From a utilitarian point of view these equations, (8) - (11), are not final in that the unknown energy E occurs in the denominator of Eq. (9)., and results in size consistency problems unless treated properly. This difficulty may be circumvented here, as in Rayleigh-Schrodinger perturbation theory, by using the first order approximation to the energy. To do this, and to solve these equations, one expands the inverse in Eq. (9) in a power series

$$T = 1 + (H_0 - w_1)^{-1} (1 - P) (E - w_1 - V) + \dots + [(H_0 - w_1)^{-1} (1 - P) (E - w_1 - V)]^n + \dots \quad (12)$$

In this case the first approximation to E is found by solving

$$(E - w_1) \pi_i = \sum_{k=1}^n \pi_k \langle \phi_i | V | \phi_k \rangle. \quad (13)$$

If this prescription is followed, if n = 1 for example, one simply recovers ordinary Rayleigh-Schrodinger Perturbation theory.

Further ramifications of the use of MR-MBPT and ordinary MBPT

have also been given by the group of Bartlett [11, 12].

In this, as in most other numerical studies, the algorithms chosen are designed first to achieve a desired level of precision and only then chosen to maximize efficiency. After all there is little value in achieving incorrect results, no matter how quickly. In these studies, we follow one of the conventional wisdoms of quantum chemistry and expand our orbitals in a basis set of gaussian orbitals. The primitive gaussian orbital is of the form:

$$\chi_{1x i j k}(\vec{r} - \vec{R}_1) = (x^i y^j z^k / r^{i+j+k}) \exp(-a_1 (\vec{r} - \vec{R}_1)^2) \quad (14)$$

This function has the advantage that all necessary integrals over these basis functions can be evaluated in closed form [10]. This allows one to know all integrals to arbitrary precision. Using this set, one may construct a "contracted" set of basis functions, $\phi_{j k}$, where

$$\phi_{j k}(\vec{r} - \vec{R}_1) = \sum_{\alpha} A_{\alpha} \chi_{\alpha i j k}(\vec{r} - \vec{R}_1). \quad (15)$$

The A 's in equation (15) are assumed given. One expands the Fock solutions in terms of these functions,

$$\psi_m^{\beta} = \sum_{i, j, k, l} C_i^{m\beta} \phi_{j k l} \quad (16)$$

The coefficients, $C_i^{m\beta}$, are found using the Roothaan method, which is in reality a simple linear variation [11]. It is this we wish to discuss. The variation is performed by recalling for a particular iteration, the β^{th} say,

$$\rho(\vec{x}, \vec{x}') = \sum_{m=occ} \phi_m^{\beta+}(\vec{x}) \phi_m^{\beta+}(\vec{x}') \\ \equiv \sum_{i,j,k,l} \xi_i(\vec{x}) \xi_j(\vec{x}') \sum_m C_{ijkl}^{m\beta} C_{i,j,k,l}^{m\beta*}$$

The sum over m is restricted to occupied orbitals and mapping indices i, j, k, l into an index i , and so forth, so that

$$\rho(\vec{x}, \vec{x}') = \sum_{ii'} \xi_i(\vec{x}) \xi_{i'}(\vec{x}') S_{ii}^{\beta} \quad (17)$$

where

$$S_{ii}^{\beta} = \sum_m C_i^{m\beta} C_i^{m\beta*}$$

β

Thus only S_{ii}^{β} changes from iteration to iteration.

The Fock problem then reduces to a matrix problem (for each iteration) of the form

$$F \phi = E D \phi. \quad (18)$$

The matrices D and F are given as:

$$D_{ij} = \langle \xi_i | \xi_j \rangle, \quad (19)$$

and

$$\begin{aligned}
 F_{ij} &= \langle \xi_i | F | \xi_j \rangle \\
 &\equiv \langle \xi_i | \left[-\frac{\hbar^2}{2m} \nabla^2 - \sum_I \frac{e^2 Z_I}{|\vec{r} - \vec{R}_I|} \right] | \xi_j \rangle \\
 &+ \left| \langle \xi_i \xi_k | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \xi_j \xi_l \rangle \right. \\
 &\left. - \langle \xi_i \xi_l | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \xi_k \xi_j \rangle \right| S_{kl}^{-1}
 \end{aligned}
 \tag{20}$$

Clearly the needed integrals merely need be evaluated once as they don't change from iteration to iteration. The only iteration dependent quantity is S_{kl} . Let us define;

$$f_{ij} = \langle \xi_i | \left[-\frac{\hbar^2}{2m} \nabla^2 - \sum_I \frac{e^2 Z_I}{|\vec{r} - \vec{R}_I|} \right] | \xi_j \rangle$$

and

$$g_{ijkl} = \langle \xi_i \xi_k | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \xi_j \xi_l \rangle.$$

Then

$$F_{ij} = f_{ij} + \sum_{kl} \left[g_{ijkl} - g_{ilkj} \right] S_{kl}^{-1}.
 \tag{21}$$

It is absolutely clear from equation (21) that each iteration is simply now a series of matrix operations followed by a matrix diagonalization.

The next step is to perform the correlation calculation. Consider the ordinary second order Rayleigh-Schrodinger case here. The second order correction to the energy is simply:

$$E^{(2)} = \sum_{i>j=occ.} \sum_{a>b=virt.} \frac{(V_{ijab} - V_{ijba})^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b},
 \tag{22}$$

where

$$\begin{aligned}
 V_{ijab} &= \sum_P C^{i\beta}_P \sum_r C^{j\beta}_r \sum_q C^{a\beta}_q \sum_s C^{b\beta}_s g_{pqrs} \\
 &= \langle \phi_i^\beta \phi_j^\beta | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \phi_a^\beta \phi_b^\beta \rangle
 \end{aligned}
 \tag{23}$$

The coefficient C_p is the coefficient of the basis function in the i th Fock orbital for the β^{+n} configuration. Thus the dominant correlation problem becomes one of rotating integrals over basis functions to integrals over Fock orbitals. This again is simply a series of matrix-like steps. General considerations for programming equation (21), (22) and (23) may therefore be given.

The matrix of integrals over basis functions, g_{pqrs} , is sparse (1% - 10% density). The sparseness has two causes, one being symmetry, the second being great separation of basis functions. Both considerations are taken into account before evaluating any integral, thus saving time. Once the integrals are generated one need be more particular in achieving efficiency. Consider as an example the part of the Fock matrix

$$F_{ij}^{(2)} = \sum_{kl} g_{ijkl} S_{kl}^\beta
 \tag{22}$$

or

$$F_I^{(2)} = \sum_K g_{IK} S_K^\beta
 \tag{22b}$$

In equation (22b) the indices i, j have been mapped into a single index I and k, l have been mapped into a single index K .

Computer type now enters into our consideration. In using vector computers like array processors, Cyber 205's, Cray's or

FPS164's one should avoid logic statements inside inner do loops in most cases. Therefore, the sparseness of the g matrix is of little help. It is of considerable help however, on conventional scalar-computers and one may work directly from equation (22) on such, loading only the non-zero integrals. On a vector machine however, one should use equation (22b) with the null integrals included, as each element of the Fock matrix is as seen a simple vector dot product. It is this operation which is maximally efficient on vector computers in general. Furthermore, the large length of the vector in (22b), typically of length 10^2 to 10^4 , is ideal for such systems as the Cyber 205 as well as the other vector machines. Finally, this is in good form for processing on machines with parallel architecture such as a Denelcore or FPS164/MAX, as one can use the vector S_k as a constant and work on several of the F_I 's at one time. Similar considerations apply to the matrix operations in equation (23). Thus code developments are machine specific to ensure maximum efficiency.

Recently the principal investigator has used the method of Kunz and Klein⁴ to incorporate exact boundary conditions at the Quantum cluster-Hades interface into the ICECAP formalism. This is accomplished as follows. Assume in the region beyond the Quantum cluster boundary that the first order density matrix for a given ion/atom/molecule is the same as that of the perfect solid. This first order density matrix may be trivially determined by the method of local orbitals. A program to evaluate this first order density matrix, LOPAS, has for a reasonably general case been developed by one of us (ABK) and is well described in the

literature.⁵ This then determines the entire first order density matrix in regions outside the cluster. The entire first order density matrix, ρ , is formally given as

$$\begin{aligned} \rho(\vec{x}, \vec{x}^1) &= \rho_c(\vec{x}, \vec{x}^1) + \sum_{\mu} \sum_{\substack{\mu \\ \text{not in } c}} \rho_{\mu}(\vec{x}, \vec{x}^1) + \sum_{\mu} \rho_{c\mu}(\vec{x}, \vec{x}^1) \\ &+ \rho_{c\mu}(\vec{x}, \vec{x}^1) + \sum_{\substack{\mu, z \\ \text{not in } c}} \rho_{\mu z}(\vec{x}, \vec{x}^1). \end{aligned} \quad (24)$$

Here ρ_c refers to the cluster and n or z are ion sites outside the cluster. Cross terms ρ_{μ} , $\rho_{c\mu}$, $\rho_{\mu\nu}$ occur because in Ref. 5 we exploit the generality of the local orbital prescription and use different localizing potentials for different regions. The relevant part here is

$$\begin{aligned} \rho_c(\vec{x}, \vec{x}^1) &= \sum_{\substack{i, j \\ i, j \text{ in } c}} \phi_i(\vec{x}) \phi_j(\vec{x}^1) S_{ij}^{-1} \approx \sum_{i \text{ in } c} \phi_i(\vec{x}) \phi_i(\vec{x}^1) \\ S_{ij} &= \langle \phi_i | \phi_j \rangle \\ \rho_{\mu\mu} &= \sum_{\substack{i, j \\ \text{OR } \mu}} \phi_i(\vec{x}) \phi_j(\vec{x}^1) S_{ij}^{-1} \\ \rho_{\mu\nu} &= \sum_{\substack{i, j \\ \text{OR } \mu, \nu}} \phi_i(\vec{x}) \phi_j(\vec{x}^1) S_{ij}^{-1} \\ \rho_{\mu c} &= \sum_{\substack{i, j \\ \text{OR } \mu, c}} \phi_i(\vec{x}) \phi_j(\vec{x}^1) S_{ij}^{-1} \end{aligned}$$

Now consider the general local orbitals equation for defining the ϕ 's. It is of the form

$$[F + \rho_w \rho] \phi_i = \epsilon_i \phi_i.$$

(25)

F is the Fock operator defined in Eq. 6 and ρ the first order density matrix defined here is identical to that in Eq. (5), hence

the utility of this method. For ϕ_i in c we arbitrarily chose

$$W = \rho_C V_E^S \rho_C \quad (26)$$

Here ρ_C is as given above and V_E^S is the non ionic part of the potential due to all ions/atom/molecules outside of the cluster.

Now since:

$$\rho \rho_C = \rho_C \rho = \rho$$

one finds

$$[F + \rho \rho_C V_E^S \rho_C \rho] \phi_i = \epsilon_i \phi_i, \quad (27)$$

becomes

$$[F + \rho_C V_E^S \rho_C] \phi_i = \epsilon_i \phi_i \quad (28)$$

This is exact and defines all ϕ_i in the cluster C . Thus the added term $\rho_C V_E^S \rho_C$ in the Fock equation replaces the crystal outside of C . Since the term V_E^S is determined in this method self consistently and can contain even the contributions of an infinite crystal, this approach completely solves the problem of the cluster boundary condition. Current efforts are directed at implementing this equation into ICECAP. Preliminary tests of ICECAP on molecular/energetic solids should be made early in 1985.

Some Preliminary Results

F and F_A centre properties (optical absorption, hyperfine constants, and spin polarization) in alkali halides were investigated in 1980 by Kung et al. [13], with a nearest-neighbour UHF-SCF cluster based on free-atom orbitals, neglecting lattice distortion and polarization. For the first time, the F_A -centre absorption splitting was described correctly, and other encouraging results were obtained for these electrically neutral

defects, although the smallness of the cluster was recognized as a problem.

Recently, we have analysed the F^+ centre in MgO [14], a charged defect, including multipole consistency, based on HADES, and using ATMOL [15] rather than Kunz's UHF [4] for the cluster. In the course of this work we came to recognize the need for complete-ion pseudopotentials, or some other form of frozen extended ions, at the cluster boundary. Nevertheless, the crucial importance of correct, consistent treatment of polarization in optical absorption, and of the ion-size effect in emission, were demonstrated, and partial electron transfer (hole trapping) in absorption was illustrated.

These methods apply directly to spectroscopic computation. A recent series of such studies have been made by Goalwin and Kunz [16] for atoms, molecules, and solid excitons. In the case of the excitons, the change in electronic structure in the cluster is of a quadrupole nature and hence outside the cluster the continuum dielectric limit is adequate and included here.

The results of this investigation are tabulated in Table 1. The energy levels calculated in the UHF+MBPT+polarization approximation appear to be within .2 ev. of the experimental levels for all atomic and molecular cases. Singlet-triplet splittings appear to be accurate to within .1 ev.

One point frequently brought up in connection with the UHF method is that triplet wavefunctions are not eigenstates of S^2 . Our calculated values of the spin in the triplet state were between 1.0000 and 1.0005 for atomic cases, 1.01 for methane, and

between 1.000 and 1.002 for the alkali halides. Since S_z is chosen equal to 1 it seems reasonable to identify these states as triplet, since it is unlikely that a mixture of eigenstates of S^2 with substantial contributions from states with eigenvalues of S^2 greatly different from 2 would give a value of S so close to the expected value for a pure triplet state. The triplet and contaminated singlet states from VHF form a system which is rediagonalized to permit formation of pure singlet systems here.

The levels hypothesized to be the result of a $3p^24s$ exciton in the alkali halides have energies and singlet-triplet splittings close to the levels theoretically predicted for such states. The shoulder in the NaCl data that peaks at 10.3 ev. could be caused by a $3p^23d$ exciton, as the theoretically predicted energies for those states lie in the region covered by the shoulder.

The splitting of the calculated energy levels for the $3p^23d$ exciton in KCl is smaller than in NaCl and the observed peak in KCl is narrower. However, the energy observed is .7 ev to 1.0 ev. higher than the calculated energy. It is possible that this is due to the unusually low correlation energy of about 0.04 Hartrees obtained with this basis set. It would be difficult to increase the size of the basis set and still do the calculation on the computers available to us. It is also possible that the computed 3d level refers to the first d level possible in the excited state as the present use of the variational principle would imply. In such a case, the narrow peak identified as a d-level in the absorption spectra could well be an accumulation point for the p to d transition series limit. It seems to us that the latter explanation is likely.

No variational collapse for the excited states is observed in any of these systems. Our computed value for the He 1s2s singlet energy is 0.7562 Hy. Fraga and Briss [17] obtain .7461 Hy. Other workers [18, 19] have not reported the ground state energy they obtain but give absolute energies for the excited state comparable to our result.

Polarisation and Distortion of the Surrounding Lattice: The HADES Code

The HADES code is based on the general formulation for treating the defective lattice developed by Lidiard and Norgett (20) and Norgett (21). It relies on the idea that the total energy of the system is minimized by a relaxation of the ions surrounding the defect and that this relaxation decreases rapidly as the distance from the defect increases. We may therefore partition the crystal into an inner region I in which the lattice configuration is evaluated explicitly and an outer region II that can be viewed from the defect as a continuum. The total energy of the system may then be written as

$$E = E_I(\underline{x}) + E_{int}(\underline{x}, \underline{\xi}) + E_{II}(\underline{\xi})$$

in which $E_I(\underline{x})$ is the energy of the inner region, $E_{II}(\underline{\xi})$ the energy of the outer region and $E_{int}(\underline{x}, \underline{\xi})$ the interaction energy between regions I and II. \underline{x} is a vector of the independent coordinates describing the inner region and $\underline{\xi}$ is a corresponding vector of the displacements in the outer region. $\underline{\xi}$ is both formally distinguished from \underline{x} and assumed to be an implicit function of it, though in practice $\underline{\xi}$ is usually calculated from the position and charge of the defect using a continuum

approximation.

We may eliminate the outer crystal term $E_{II}(\xi)$ by assuming that the outer region responds harmonically and so $E_{II}(\xi)$ is a quadratic function of ξ . Applying the equilibrium condition

$$\frac{\partial E}{\partial \xi} = 0$$

then allows us to eliminate $E_{II}(\xi)$.

In principle, we may now find the defect energy by applying a force balance condition to the ions in the inner region i.e.

$$\left. \frac{\partial E}{\partial x} \right|_{\xi = \text{constant}} = 0$$

To proceed further we require an explicit representation of the energy E . We assume this to be the sum of two-body interactions. Details of how this is implemented in the HADES program and of the minimization procedures used to obtain the force-balance position are given in references (21) and (22).

The HADES code and its extensions have been used as the basis of several hundred papers concerning defect behaviour in ionic crystals. Extensions to treat defects at surfaces and interfaces (like grain boundaries, etc.) already exist, and may be used in later phases.

Some specific progress in implementing these ideas for systems such as CH_4 , $(\text{NO})_2$ and nitromethane has been achieved and will be reported in an interim technical report shortly. Nonetheless, the general thrust of the past year has been directed toward a general implementation of these rather comprehensive ideas for studies on defects and impurities.

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TABLE 1

SUMMARY OF RESULTS
 (ALL ENERGIES ARE IN ELECTRON-VOLTS)
 (T triplet, S singlet)

MATER. IAL	STATE	UHF ENERGY	TOTAL ENERGY	EXPERIMENTAL ENERGY
He	1s2sT	19.04	19.8	19.81
He	1s2sS	19.88	20.58	20.61
Be	2s3sT	5.69	6.35	6.46
Be	2s3sS	6.00	6.56	6.78
B	2s23s	4.89	4.90	4.96
B	2s23p	5.92	5.84	6.003
Ne	2p53sT	15.00	16.44	16.15
Ne	2p53sS	15.18	16.75	16.8A
Ne	2p53pT	16.78	18.33	-
Ne	2p53pS	17.27	18.56	-
CH4	1s3sT	286.68	286.88	287.2
CH4	1s3sS	287.03	287.27	287.2
CH4	1s3pT	287.92	288.11	288.3
CH4	1s3pS	288.06	288.24	288.3
NaCl	3p54sT	8.33	8.02	7.9
NaCl	3p54sS	8.51	8.30	8.1
NaCl	3p53d(xy)T	9.59	10.22	10.3
NaCl	3p53d(xy)S	9.62	10.26	10.3
NaCl	3p53d(zz)T	9.23	9.62	10.3
NaCl	3p53d(zz)s	9.25	9.64	10.3
KCl	3p54sT	7.84	7.62	7.8
KCl	3p54sS	7.98	7.76	7.9
KCl	3p53d(xy)T	8.89	8.86	9.5
KCl	3p53d(xy)S	8.91	8.82	9.5
KCl	3p53d(zz)T	8.25	8.54	9.5
KCl	3p53d(zz)S	8.29	8.64	9.5

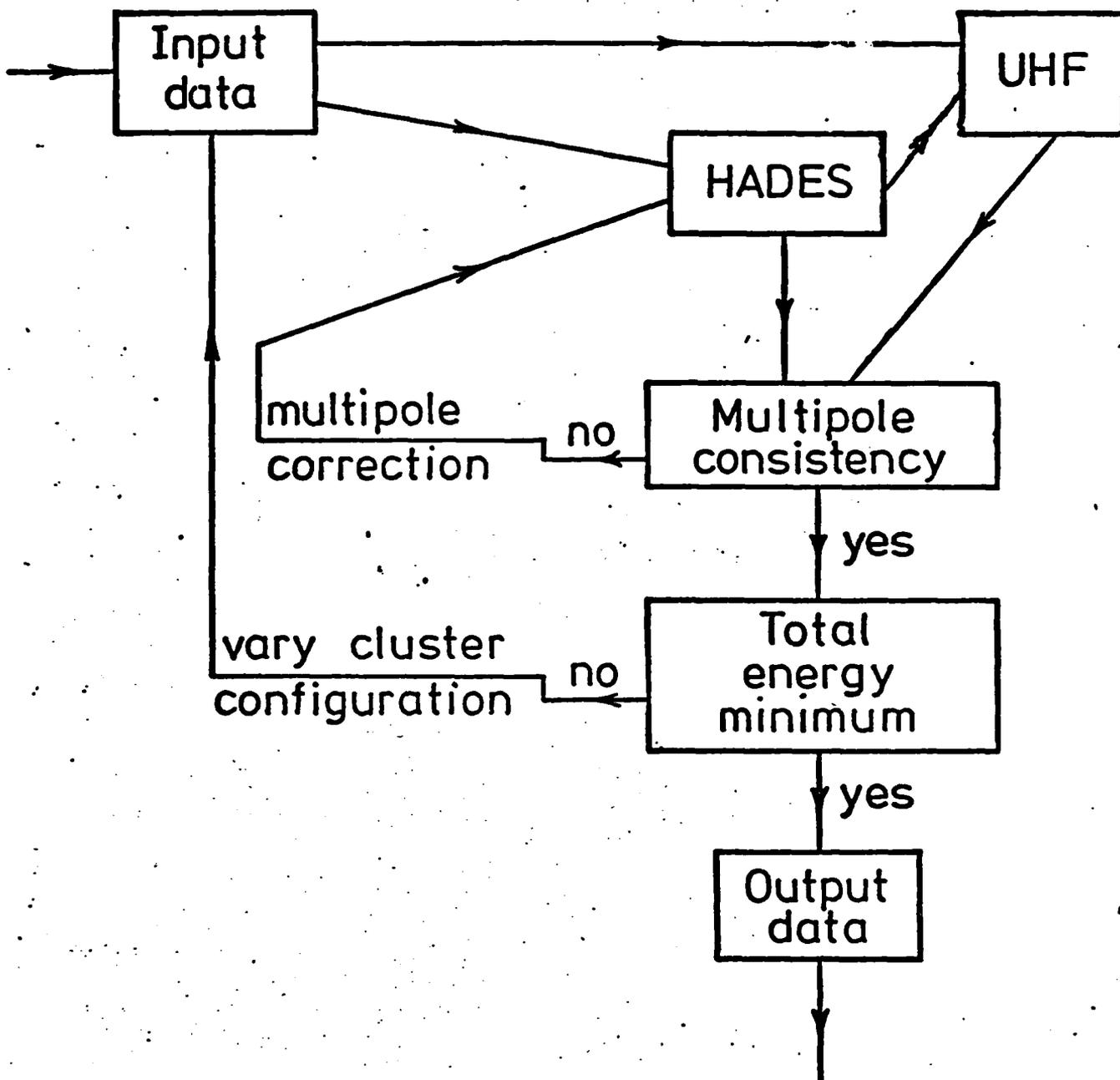


FIG. 1.

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A. B. KUNZ - Invited Papers

- 1969 29 September to 4 October, European Congress on Molecular Spectroscopy, "Energy Band Structure and Optical Properties of Four Alkali Fluorides", Universite' de Liege, Belgium.
- 1972 4 July, International Conference on Electron Energy Structure, "Ab Initio Energy Band Studies for Ionic Solids", University of Exeter, England.
- 1973 18-30 June, NATO, Advanced Study Institute, On Elementary Excitations in Solids, Molecules and Atom. Two Lectures:
 - "Ab Initio Energy Band Methods"
 - "Soft X-ray Spectra of Molecules".

27-29 December, APS winter meeting at Berkeley, "Soft X-ray Spectra of Insulating Solids", University of Berkeley, California.
- 1974 January, International Symposium on Quantum Theory of Atoms, Molecules, and the Solid-State. "Many-Body Effects in Energy Band Theory", Sanibel Island, Florida (University of Florida).

- 22-26 July, IV International Conference on Vacuum Ultraviolet Radiation Physics, "Calculation of Optical Absorption Edges and Photo-Emission Edges in Solids", Hamburg, Germany.
- 17-18 November, Midwest Solid State Theory Symposium, "Photo-Emission Studies of Insulating Solids", Indiana University.
- December, Peat Symposium of the U.S. Geological Society, in cooperation with T. L. Phillips and D. J. Michish, "Paleobotany of Petrified Peak (Coal Ball) Coal Member of the Illinois Basin", Miami Beach, Florida.
- 1975 23-27 June, Summer Research Conference in Theoretical Chemistry, Session Chairman on Subject of Ab Initio Theory of Crystal and Surface Science,* Boulder, Colorado.
- 15 July to 15 September, "Centre European de Calcul Atomique et Maelculaire, Workshop on Ab-initio one-electron potentials". Seminar series declined, Orsay, France.
- 1976 18-24 January, International Symposium on the Quantum Theory of Atoms, Molecules and the Solid-State; Symposium Leader; Sanibel Island, Florida.
- 9-13 August, Gordon Conference on Atomic and Molecular Interactions.
- 1977 5 November, Midwest Solid State Theory Meeting, Argonne Nat. Lab., declined due to conflict.
- 1978 4-18 June, NATO ASI, Excited States in Quantum Chemistry, KOS, Greece.
- 1979 17 March, Int. Symp. on Quantum Chemistry, Electronic Properties of CuCl, Palm Coast, Florida.
- 25 August, Sagamore Conference on Crystallography, Mt. Tremblant, Canada.
- 1980 15 March, International Sym. on Quantum Chemistry, Recent Developments in CuCl and CdS, Palm Coast, Florida.
- 22 March, IBM Workshop on Effective One-Electron Potentials. Electronic Structure of Transition Metal Oxides, Ossining, New York.
- 1-4 July, Gordon Conference on Electron Distribution and Chemical Bonding - discussion leader.
- 1981 21 January, Workshop on Fundamental Research on Energetic Materials, Finite Cluster Techniques for Modeling Extended

Systems, Berkeley, California.

14 March, International Symposium on Quantum Chemistry, Palm Coast, Florida. Fundamental Properties of Narrow Band Materials.

June, Symposium of NRCC, Los Alamos. Two invited talks:
1. Simulation of Extended Systems by Finite Clusters
2. Solid State Effective Potentials

1982 May, DOD Workshop on Energetic Materials: Properties of Energetic Solids and Molecular Crystals.

1983 12 March, Sanibel Symposium on Impact of Computers on Quantum Chemistry and Solid State Computations - Panel.

24 July - 5 August, "Excited States in Molecular Solids, Collective Effects", NATO ASI, Braunlage, West Germany on Quantum Theory of Polymers, Solid State Aspects.

9 August, "Energy Transfer, Trapping and Release in Molecular Crystals and Energetic Solids", DOD Workshop on Energetic Materials, Great Oaks, Maryland.

3 October, "The Electronic Structure of Impurities and Defects in Simple Metals", Fall Meeting of the Metallurgical Society and the American Society of Metals.

1984 1-10 March, Sanibel Symposium, Parts I and II, Organizing Committee for Part I and Session Chairman.

9-13 April, Royal Society of Chemistry, London, England; Invited Plenary Lecture: "Chemisorption and the Electronic Structure of Transition Metal Oxides and Transition Metals Bonded to Oxide Surfaces".

6-10 August, Department of Energy Panel on Simulation and Theory of Defect Structures in Solids ---, Chairman and organizer.

5-8 September, Midwest Solid State Theory Conference, Minneapolis, Minnesota, "Defect Simulation and Super Computers".

30 October - 1 November, Annapolis, Maryland, DoD Workshop on Energetic Materials Initiation Fundamentals, "ICECAP Approach to Impurity and Defect Problems".

*These sessions consist of a few short invited talks and an extemporized program.

National Bureau of Standards
Aerospace Research Laboratory, Wright-Patterson AFB
Brookhaven National Laboratory

Argonne National Laboratory
Oak Ridge National Laboratory
Bell Telephone Laboratories (Murray Hill)
Bell Telephone Laboratories (Holmdale)
Eastman-Kodak Company
E. I. Dupont de Nemours Company
Belgian Atomic Energy Establishment-Moll
University of Liege
Lehigh University
Drexel Institute of Technology
Battelle Memorial Institute
Queens College CUNY
University of North Carolina
Wake-Forest University
University of Georgia
Stanford University
Arizona State University
Oklahoma State University
University of Illinois
Indiana University
Purdue University
Louisiana State University (Baton Rouge)
University of Manitoba
Texas A & M University
Naval Research Laboratories
U. S. Army Ballistics Research Laboratory, Aberdeen, Maryland
Michigan State University
Hirman College
General Motors Corporation
Michigan Technological University
Air Force Avionics Laboratory
University of Missouri, Columbia
University of Missouri, St. Louis
University of Missouri, Rolla
Los Alamos National Laboratory
University of New Orleans
Johns Hopkins University
University of Florida

D. R. Beck - Publications in Referred Journals for 1980 to present. Those preceded by an * denote DNR support.

42. D. R. Beck and C. A. Nicolaides, "On the Theoretical Interpretation and Calculation of Inner Photoemission Spectra in Atoms and Solids", Int. J. Quant. Chem. S14, 323 (1980).
43. D. R. Beck, "Many Electron Effects in and Operator Forms for Electron Quadrupole Transition Probabilities", Phys. Rev. A23, 159 (1981).
44. C. A. Nicolaides, Y. Komninos and D. R. Beck, "Bound States and Decay Mechanisms of He⁻", Phys. Rev. A24, 1103 (1981).

45. D. R. Beck, "On the Incorporation of Local Correlation Effects Into Ionic Solids", Int. J. Quant. Chem. S15, 521 (1981).
46. D. R. Beck, C. A. Nicolaides, and G. Aspromallis, "The Spectrum of the Negative Be Ion", Phys. Rev. A24, 3252 (1981).
47. D. R. Beck and C. A. Nicolaides, "Specific Correlation Effects in Inner Electron Photoelectron Spectroscopy", Phys. Rev. A26, 857 (1982).
48. D. R. Beck, "On the Spectrum of Negative Ions and the Charge Density of the Ground State of Neutral Neon", Int. J. Quant. Chem. S16, 345 (1982).
49. A. R. Slaughter, R. D. Mathews, R. S. Key, M. J. Banna, and D. R. Beck, "An Experimental and Theoretical Study of the $3P_{3/2}$ Level of Atomic Desium: Beyond the One-Electron Picture", J. Chem. Phys. 77, 1690 (1982).
50. C. A. Nicolaides, Y. Komninos, and D. R. Beck, "Many Electron Theory of Discrete-Discrete and Discrete-Continuum Transition Rates for Systems with Symmetry", Chimica Chronika (Greece), New Series, 10, 35 (1981).
51. D. R. Beck, "A New Bound State of the Negative B Ion", Phys. Rev. A27, 1197 (1983).
52. C. A. Nicolaides, Y. Komninos, and D. R. Beck, "The K-Shell Binding Energy of Be and Its Fluorescence Yield", Phys. Rev. A27, 3044 (1983).
53. G. Aspromallis, C. A. Nicolaides, and D. R. Beck, "Probabilities for Transition Processes Crucial to Li Lasers", Phys. Rev. A28, 1897 (1983).
54. D. R. Beck and C. A. Nicolaides, "Lifetime and Hyperfine Structure of Li- Excited States", Phys. Rev. A28, 3112 (1983).
55. D. R. Beck and C. A. Nicolaides, "Electric Quadrupole Transition Probabilities for the Lowest 1D Metastable State in Ca and Sr", J. Phys. B, in press.
56. D. R. Beck, R. J. Key, A. R. Slaughter, R. D. Mathews, and M. S. Banna, "Atomic and Molecular 2p Binding Energies of P, As, and Se from Many-Body Calculations and X-Ray Photoelectron Spectroscopy", Phys. Rev. A29, 2634 (1983).

- *57. D. R. Beck and A. B. Kunz, "Excitation Energies for the Lowest Triplets and Singlet-Triplet Splittings in Gas Phase Methane Including Many Body Effects", J. Phys. B17, 2159 (1984).
- 58. K. T. Cheng, J. E. Hardis, E. J. Dehm and D. R. Beck, "Fine and Hyperfine Structure of the Li- Spectrum", Phys. Rev. A30, 698 (1984).
- 59. D. R. Beck and C. A. Nicolaides, "Fine and Hyperfine Structure of the Two Lowest Bound States of Be- and Their First Two Ionizations Thresholds", Int. J. Quantum Chem. Suppl. for 1984, accepted.
- 60. D. R. Beck, "The Three Lowest Bound States of Mg-", Phys. Rev. A30, 3305 (1984).
- 61. D. R. Beck, "K-Shell Binding Energy of Mg and Ca", J. Chem. Phys., accepted.
- 62. G. Aspromalis, C. A. Nicolaides, and D. R. Beck, "Relativistic Autoionization of Bound States of Negative Ions, I: Be-". Phys. Rev. A. Accepted for publication.

D. R. BECK - Other Selected Publications, etc.

- 15. D. R. Beck and A. B. Kunz, "On the Calculation of Optical Spectra of Color Centers in Alkali Halides by Self-Consistent Pseudopotential Methods", Bull. Am. Phys. Soc. 25, 186 (1980).
- 16. A. B. Kunz and D. R. Beck, "The Hartree-Fock Approach and Beyond", IBM Workshop on Effective One-Electron Potentials for Real Materials, Ossining, New York, March 21-22, 1980.
- 17. D. R. Beck, "On the Persistence of Non-Relativistic Correlation Effects in Relativistic Atoms", in Relativistic Effects in Atoms, Molecules and Solids, G. Malli, Editor, Plenum Press (1983), p. 502 (abstract only).

D. R. Beck - Participant or Speaker at the Following Conferences

New Directions in Atomic Physics, Smyrna, 1969
 Gordon Conference on Atomic Physics, Amherst, New Hampshire
 Third International Conference on Atomic Physics, Boulder, Colorado
 International Symposium on Quantum Theory of Atoms, Molecules, and the Solid State, Sanibel Island (1974, 1976, 1981, 1982) ("Symposium Leader" in 1981 and 1982)
 Ninth Annual Symposium on Quantum Chemistry, Atomic and Molecular Physics, Yeshiva University (organizer)
 Fourth International Beam Foil Conference, Gatlingberg, Tennessee

Atomic Spectroscopy Symposium, National Bureau of Standards, Gaithersburg, Maryland, 1975

NATO Advanced Study Institute on Polymers, Namur, Belgium, 1977

NATO Advanced Study Institute on Excited States of Atoms, Molecules and Solids, Kos, Greece, 1978 (co-organizer, speaker)

NATO Advanced Study Institute on Relativistic Effects in Atoms, Molecules and Solids, Vancouver, Canada, 1981

ONR Workshop in Energetic Materials, Chestertown, Maryland, 1982

D. R. Beck - Invited Lectures, Colloquia

Yeshiva University

Yale University

Pennsylvania State University

Freie Universitat Berlin

Lehigh University

Los Alamos Laboratory

Adelphi University

Argonne National Laboratory

University of Florida

University of Illinois at Urbana-Champaign

NATO Institute on Kos (1978)

Present Research Support of A. B. Kunz and D. R. Beck.

1. Energy Trapping, Release and Transport in Three Dimensional Energetic Solids, A. Barry Kunz, Principal Investigator, Office of Naval Research, awarded, N00014-81-K-0620, 1 July 1981-30 June 1986, total award \$345,768.00. Current annual level, \$75,000.00.
2. Properties of Bound States of Transition Metal Negative Ions, D. R. Beck, Principal Investigator, National Science Foundation, pending, 1 October 1985-30 September 1987, total request \$58,041.
3. Development of Ab-Initio Molecular Potentials for Certain Natural Gas Constituents, D. R. Beck, Principal Investigator, Gas Research Institute, pending, 1 January 1986-31 December 1988, total request \$142,500.
4. Theory of Defects in Non-Metallic Solids, A. B. Kunz,

principal investigator, U. S. Department of Energy, pending, 1
July 1985-30 June 1988, total request is \$380,887.00.

Graduate Students Supported by this Grant and anticipated Degree
date:

1. Christopher Woodward, June 1985
2. David Groh, June 1986
3. David Lucas, June 1986

No unexpended funds will remain in this contract at the end of the
contract period.

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